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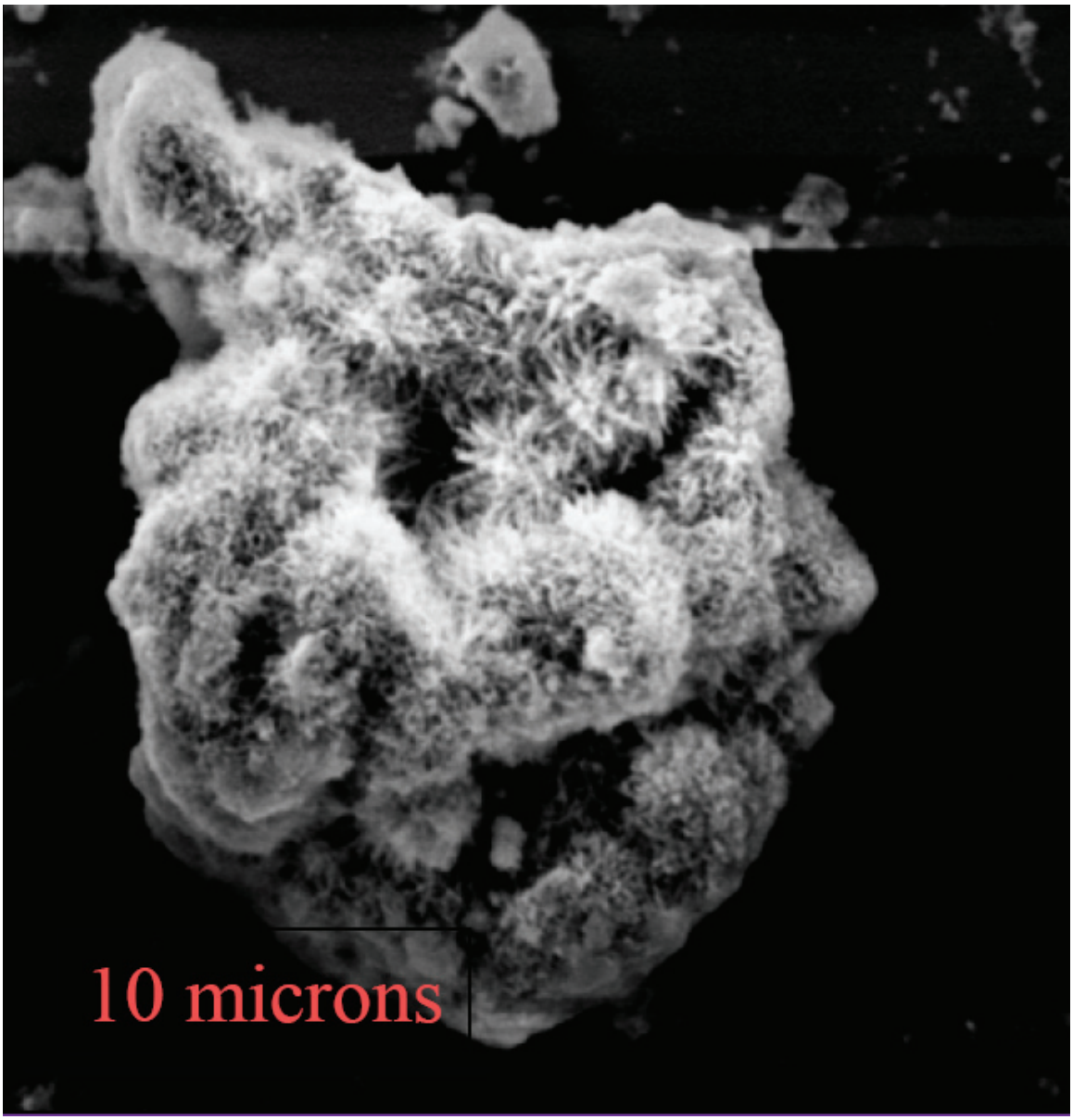

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An efficient solution for the single-step synthesis of $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ powders

Author(s):
Robert Ianos

Single-phase nanocrystalline $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ powders were prepared directly from the combustion reaction using a new cost-effective, time-saving, and environmentally friendly version of solution combustion synthesis. Instead of a single fuel, a fuel mixture of urea and ß-alanine was used. It was shown by x-ray diffraction, energy-dispersive x-ray analysis, thermogravimetric analysis, and optical microscopy that this new version of the solution combustion synthesis allows the maximization of the exothermic effect associated with the combustion reaction. On the other hand, it was shown that the traditional version of combustion synthesis involving the use of a single fuel, such as urea or ß-alanine, does not ensure the formation of $Ca_4Al_2Fe_2O_{10}$ unless subsequent thermal treatments are applied. It was suggested that the occurrence of combustion reactions cannot be regarded only in terms of adiabatic temperature, as the kinetic aspects overrule the thermodynamic ones.

Heating of alanine with urea afforded polyalanine containing a hydantoin ring at the *N*-terminal position. Molecular weight of the polymer was lower than 8000, as estimated by dialysis of the product. Molten urea was considered to facilitate spontaneous polymerization of alanine as well as to act as a dehydrating agent.

Revision date: 9/11/ 2009

Draft Technical Guidelines on Co-processing of Hazardous Waste in Cement Kilns

By adopting a feasible microwave-induced solution combustion synthesis (MISCS) method, pure and well-crystallized $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) nanoscale blue phosphors were successfully prepared. The crystallinity, particle size, morphology, chemical composition and luminescent properties were characterized by XRD, FE-SEM, EDS and spectrofluorometer, respectively. The results show that the obtained BAM phosphors have spherical morphology, good crystallinity, and strong blue emission under vacuum ultraviolet (VUV) light excitation compared to those prepared by conventional solution combustion method.

Solution combustion synthesis for catalytic and power generation applications

Peter Riising Erri[2]

Abstract

The solution combustion technique is a novel synthesis method which enables rapid synthesis of highly substituted oxides. In the procedure, the metal precursors (typically in the form of nitrates serving as oxidizers), mixed in water with fuel (e.g. hydrazine or glycine), are heated, resulting in self-ignition to yield complex oxides in a one-step process. The advantages of this technique include reactant mixing at the molecular level, and the unique ability to tailor product structural characteristics by varying parameters such as fuel and oxidizer ratio and composition. In this work, the application of this synthesis method in the following research directions will be discussed: (1)Â One-step synthesis of transition metal foams. Solution combustion synthesis was, for the first time, applied to metal foam formation. The reaction parameters were optimized to produce metal structures with no need for further reduction. (2)Â Development of coking resistant catalysts for autothermal reforming of JP-8 fuel. In this project, a novel complex oxide catalyst was developed with excellent reactivity (equilibrium conditions attained in 30 ms) and strong coking resistance. (3)Â Study of oxygen carriers for chemical looping combustion. A novel approach to combustion for power generation, this concept enables inherent separation of CO2 , while using air as an oxidant, but is limited by the lack of suitable oxygen carriers. In this context, NiO, supported with a doped spinel phase, was evaluated and found to possess excellent redox and mechanical characteristics suitable for chemical looping combustion. The findings from the three research projects illustrate the versatility of the solution combustion technique and its value as a synthesis method in catalysis and materials research.

Revision date: 9/11/ 2009

Preamble

These technical guidelines provide general guidance on co-processing of waste as alternative fuels and raw materials in cement production in accordance with provisions of the Basel Convention.

The Basel Convention emphasizes, amongst other principles, environmentally sound management (ESM) of hazardous and other wastes, which is defined as taking all practicable steps to ensure that hazardous and other wastes are managed in a manner that will save natural resources, and will protect human health and the environment against the adverse effects which may result from such wastes. The Basel Convention requires that Parties take the appropriate measures to "ensure the availability of adequate disposal facilities, for the environmentally sound management of hazardous wastes and other wastes, that shall be located, to the extent possible, within it, whatever the place of their disposal" and to "ensure that the transboundary movement of hazardous wastes and other wastes is reduced to the minimum consistent with the environmentally sound and efficient management of such wastes". Countries should therefore strive for greater self-sufficiency in hazardous waste management where this is technically and economically feasible

Co-processing of waste materials in properly controlled cement kilns provides energy and materials recovery while cement is being produced and offers a safe disposal option for many of society's wastes. Particularly in developing nations, which may have little or no waste management infrastructure, properly designed and operated cement kilns can provide a practical, cost-effective and environmentally preferred option (in line with the Waste Management Hierarchy) to landfill and incineration, through the co-processing of waste materials. Co-processing of waste in the resource-intensive industries in general, can be an important element in a more sustainable system of managing raw materials and energy.

Although the substitution of fossil fuels with alternatives is viewed by some stakeholders and jurisdictions in the same light as incineration, it is nevertheless a well-developed practice in a number of countries, and some national governments actively promote this approach, provided that stringent requirements with regard to input, process and emission control are met.

These guidelines are considered to be current best practice at the time of writing and should not be regarded as providing a conclusive indication of appropriate action. Neither should they be regarded as prescriptive or a clear recommendation to use an option in all cases. They provide a general orientation concerning the conditions in which co-processing can be applied and will require regular update in order to incorporate advances as they arise.

These technical guidelines refer to both hazardous and non-hazardous waste, although the emphasis is on the former as defined by the Basel Convention. These guidelines do not cover quarrying or the re-use of concrete, nor the substitution of blast furnace slag (recycled from steel production) and fly ash (recovered from coal driven power stations) for clinker.

Glossary

Accuracy: A measure of the overall agreement of a measurement to a known value; includes a combination of random error (precision) and systematic error (bias) components of both sampling and analytical operations.

Aggregates: Particulate materials such as sand, gravel, crushed stone, and crushed slag, used in construction.

Alkali bypass: A duct between the feed end of the kiln and the preheater tower through which a portion of the kiln exit gas stream is withdrawn and quickly cooled by air or water to avoid excessive build-up of alkali, chloride and/or sulphur on the raw feed. This may also be referred to as the 'kiln exhaust gas bypass'.

Alternative fuels and raw materials (AFR): Inputs to clinker production derived from waste streams that contribute energy and/or raw material.

Alternative fuels: Wastes with recoverable energy value used as fuels in a cement kiln, replacing a portion of conventional fossil fuels, like coal. These are sometimes termed secondary, substitute or waste-derived fuels, among others.

Alternative raw materials: Wastes containing useful minerals such as calcium, silica, alumina, and iron used as raw materials in the kiln, replacing raw materials such as clay, shale, and limestone. These are sometimes termed secondary or substitute raw materials.

Audit: A systematic and independent examination to determine whether quality activities and related results comply with planned arrangements and whether these arrangements are implemented effectively and are suitable to achieve objectives.

Best available techniques (BAT): The most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.

Bypass dust: Discarded dust from the bypass system dedusting unit of suspension preheater, precalciner and grate preheater kilns, consisting of fully calcined kiln feed material.

Calcination: The heat-induced removal, or loss, of chemically-bound volatiles, usually other than water. In cement manufacture it involves the thermal decomposition of calcite (calcium carbonate) and other carbonate minerals to a metallic oxide (mainly CaO) plus carbon dioxide.

Cement kiln dust (CKD): The fine-grained, solid, highly alkaline material removed from cement kiln exhaust gas by air pollution control devices. Much of the material comprising CKD is actually unreacted raw material, including raw mix at various stages of burning and particles of clinker. The term CKD is sometimes used to denote all dust from cement kilns, i.e. also from bypass systems.

Cement: Finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability under water.

Clinkering: The thermochemical formation of the actual clinker minerals, especially to those reactions occurring above about 1300°C; also the zone in the kiln where this occurs. Also known as sintering or burning.

Comparability: A qualitative term that expresses the measure of confidence that one data set can be compared to another and can be combined for the decision(s) to be made.

Completeness: A measure of the amount of valid data needed to be obtained from a measurement system.

Concrete: Building material made by mixing a cementing material (such as portland cement) along with aggregate (such as sand and gravel) with sufficient water and additives to cause the cement to set and bind the entire mass.

Conventional (fossil) fuels: Non-renewable carbon-based fuels traditionally used by the cement industry, including coal and oil.

Co-processing: The use of waste materials in manufacturing processes for the purpose of energy and/or resource recovery and resultant reduction in the use of conventional fuels and/or raw materials through substitution.

Destruction and removal efficiency (DRE): Efficiency in destruction and removal of a given organic compound. Mathematically, DRE is calculated as follows:

$$\text{DRE} = [(W_{\text{in}} - W_{\text{out stack}})/W_{\text{in}}] \times 100$$

where W_{in} is the mass feed rate of one principal organic hazardous constituent (POHC) in the waste stream fed to the kiln, and $W_{\text{out stack}}$ is the mass emission rate of the same POHC in the exhaust emissions prior to release to the atmosphere.

Destruction efficiency (DE): A measure of the percentage of a given organic compound that is destroyed by the combustion process. Mathematically, DE is calculated as follows:

$$\text{DE} = [(W_{\text{in}} - W_{\text{out combustion chamber}})/W_{\text{in}}] \times 100$$

where W_{in} is the mass feed rate of one principal organic hazardous constituent (POHC) in the waste stream fed to the kiln, and $W_{\text{out combustion chamber}}$ is the mass emission rate of the same POHC leaving the kiln (upstream of all air pollution control equipment). The DE represents the fraction of the organics entering a kiln which is actually destroyed; the DRE represents the fraction of the organics entering a kiln which is emitted.

Disposal: Any operation specified in Annex IV to the Basel Convention ("Disposal operations")

Dry process: Process technology for cement production. In the dry process, the raw materials enter the cement kiln in a dry condition after being ground to a fine powder (raw meal). The dry process is less energy consuming than the wet process, where water is added to the raw materials during grinding to form a slurry.

Emissions testing: Manual collection of stack gas sample(s), followed by chemical analysis to determine pollutant concentrations.

Environmentally sound management (ESM): Taking all practicable steps to ensure that hazardous wastes or other wastes are managed in a manner which will protect human health and the environment against the adverse effects which may result from such wastes.

Hazardous wastes: Wastes that belong to any category contained in Annex I to the Basel Convention ("Categories of wastes to be controlled"), unless they do not possess any of the characteristics contained in Annex III to the Convention ("List of hazardous characteristics"): explosive; flammable liquids; flammable solids; substances or wastes liable to spontaneous combustion; substances or wastes which, in contact with water, emit flammable gases; oxidizing; organic peroxides; poisonous (acute); infectious substances; corrosives; liberation of toxic gases in

contact with air or water; toxic (delayed or chronic); ecotoxic; capable, by any means, after disposal, of yielding another material, e.g. leachate, which possesses any of the other characteristics.

Heating (calorific) value: The heat per unit mass produced by complete combustion of a given substance. Calorific values are used to express the energy values of fuels; usually these are expressed in megajoules per kilogram (MJ/kg).

Higher heating (calorific) value (HHV): Maximum amount of energy that can be obtained from the combustion of a fuel, including the energy released when the steam produced during combustion is condensed. It is sometimes called the gross heat value.

Hydraulic cement: A cement that sets and hardens by chemical interaction with water and that is capable of doing so under water.

Kiln line: The part of the cement plant that manufactures clinker; comprises the kiln itself plus any preheaters and precalciners, plus the clinker cooler apparatus.

Kiln: The heating apparatus in a cement plant in which clinker is manufactured. Unless otherwise specified, may be assumed to refer to a rotary kiln.

Life Cycle Assessment (LCA): objective process to evaluate the environmental burdens associated with a product, process or activity by identifying and quantifying energy and materials used and wastes released to the environment, to assess the impact of those energy and materials uses and releases to the environment, and to evaluate and implement opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing extracting and processing raw materials; manufacturing, transportation and distribution; use, reuse and maintenance; recycling and final disposal.

Lower heating (calorific) value (LHV): The higher heating value less the latent heat of vaporisation of the water vapour formed by the combustion of the hydrogen in the fuel. It is sometimes called the net heat value.

Manifest: Shipping document that travels with hazardous waste from the point of generation, through transportation, to the final disposal facility, creating a 'cradle-to-grave' tracking of the hazardous waste.

Operator: Any natural or legal person who operates or controls the installation or facility.

Portland cement clinker: A hydraulic material which consists of at least two-thirds by mass of calcium silicates ($(CaO)_3 \cdot SiO_2$ and $(CaO)_2 \cdot SiO_2$), the remainder containing aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and other oxides.

Portland cement: A hydraulic cement produced by pulverising Portland-cement clinker, and usually containing calcium sulphate.

Precalciner: A kiln line apparatus, usually combined with a preheater, in which partial to almost complete calcination of carbonate minerals is achieved ahead of the kiln itself, and which makes use of a separate heat source. A precalciner reduces fuel consumption in the kiln, and allows the kiln to be shorter, as the kiln no longer has to perform the full calcination function.

Precision: The measure of agreement among repeated measurements of the same property under identical, or substantially similar conditions; calculated as either the range or as the standard deviation. May also be expressed as a percentage of the mean of the measurements, such as relative range or relative standard deviation (coefficient of variation).

Preheater: An apparatus used to heat the raw mix before it reaches the dry kiln itself. In modern dry kilns, the preheater is commonly combined with a precalciner. Preheaters make use of hot exit gases from the kiln as their heat source.

Pre-processing: Alternative fuels and/or raw materials not having uniform characteristics (such as tyres or used oil) must be prepared from different waste streams before being used as such in a cement plant. The preparation process, or pre-processing, is needed to produce a waste stream that complies with the technical and administrative specifications of cement production and to guarantee that environmental standards are met.

Pyroprocess system: Includes the kiln, cooler, and fuels combustion equipment.

Quality assurance (QA): A system of management activities involving planning, implementation, assessment, and reporting to make sure that the end product (for example, environmental data) is of the type and quality needed to meet the needs of the user.

Quality control (QC): Overall system of operational techniques and activities that are used to fulfil requirements for quality.

Raw mix/meal/feed: The crushed, ground, proportioned, and thoroughly mixed raw material-feed to the kiln line.

Recovery: Any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy.

Representative sample: A sample of a universe or whole (for example, waste pile) which can be expected to exhibit the average properties of the universe or whole.

Representativeness: A qualitative term that expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Rotary kiln: A kiln consisting of a gently inclined, rotating steel tube lined with refractory brick. The kiln is fed with raw materials at its upper end and heated by flame from, mainly, the lower end, which is also the exit end for the product (clinker).

Trial burn: Emissions testing performed for demonstrating compliance with the destruction and removal efficiency (DRE) and destruction efficiency (DE) performance standards and regulatory emission limits; is used as the basis for establishing allowable operating limits.

Vertical shaft kiln (VSK): A vertical, cylindrical or chimney-type kiln, heated from the bottom, which is fed either with a batch or continuous charge consisting of an intimate mix of fuel and raw materials. Generally considered obsolete for cement manufacture. VSK technology is based on a black meal process, which prevents the use of alternative fuels.

Waste (management) hierarchy: List of waste management strategies arranged in order of preference, with waste prevention being the most desirable option and disposal the least preferred approach. Departing from such hierarchy may be necessary for specific waste streams when justified for reasons of, inter alia, technical feasibility, economic viability and environmental protection.

Wastes: Substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law.

Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists (http://www.acgih.org/)
ASTM	American Society for Testing and Materials (http://www.astm.org/)
BAT	Best Available Technique
BEP	Best Environmental Practice
CCME	Canadian Council of Ministers of the Environment (http://www.ccme.ca/)
CEM	Continuous Emission Monitoring Systems
CEN	European Committee for Standardization (http://www.cen.eu/)
CKD	Cement Kiln Dust
DE	Destruction Efficiency
DRE	Destruction and Removal Efficiency
EA	Environment Agency of England and Wales
EPA	United States Environmental Protection Agency (http://www.epa.gov/)
ESM	Environmentally Sound Management
GTZ	Deutsche Gesellschaft für Technische Zusammenarbeit GmbH (http://www.gtz.de/)
HAP	Hazardous Air Pollutant
ICP	Inductively Coupled Plasma
IOELV	Indicative Occupational Exposure Limit Value
IPPC	Integrated Pollution Prevention and Control
LCA	Life Cycle Assessment
MSDS	Material Safety Data Sheets
NIOSH	National Institute for Occupational Health and Safety of the United States (http://www.cdc.gov/niosh/)
OECD	Organisation for Economic Co-operation and Development (http://www.oecd.org/)
OSHA	Occupational Safety and Health Administration of the United States (http://www.osha.gov/)
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated Dibenzo-p-Dioxin
PCDF	Polychlorinated Dibenzo-Furan
PEL	Permissible Exposure Limit
PIC	Product of incomplete combustion
POHC	Principal Organic Hazardous Constituent
POP	Persistent Organic Pollutant
PPE	Personal Protective Equipment
QA	Quality Assurance
QC	Quality Control
RII	Resource-Intensive Industries
SBC	Secretariat of the Basel Convention (http://www.basel.int/)
TEQ	Toxic Equivalent
THC	Total Hydrocarbon
TLV	Threshold Limit Value
TOC	Total Organic Compounds
UNEP	United Nations Environment Programme (http://www.unep.org/)
VOC	Volatile Organic Compound
WAP	Waste Analysis Plan
WBCSD	World Business Council for Sustainable Development (http://www.wbcsd.org/)
XRF	X-Ray Fluorescence

Contents

1.Introduction

1.1. Cement Industry Overview

1. Cement is a finely ground, non-metallic, inorganic powder, which, when mixed with water forms a paste that sets and hardens. It is the key constituent of concrete, which is the second most consumed material worldwide after water. Cement production involves the heating, calcining and sintering of a carefully proportioned mixture of calcareous and argillaceous materials, usually limestone and clay, to produce cement clinker, which is then cooled and ground with additives such as gypsum (a setting retardant) to make cement. The most widely used production process for Portland cement clinker is the dry process, which is gradually replacing the wet process. The manufacturing process is described in more detail in Annex 1.

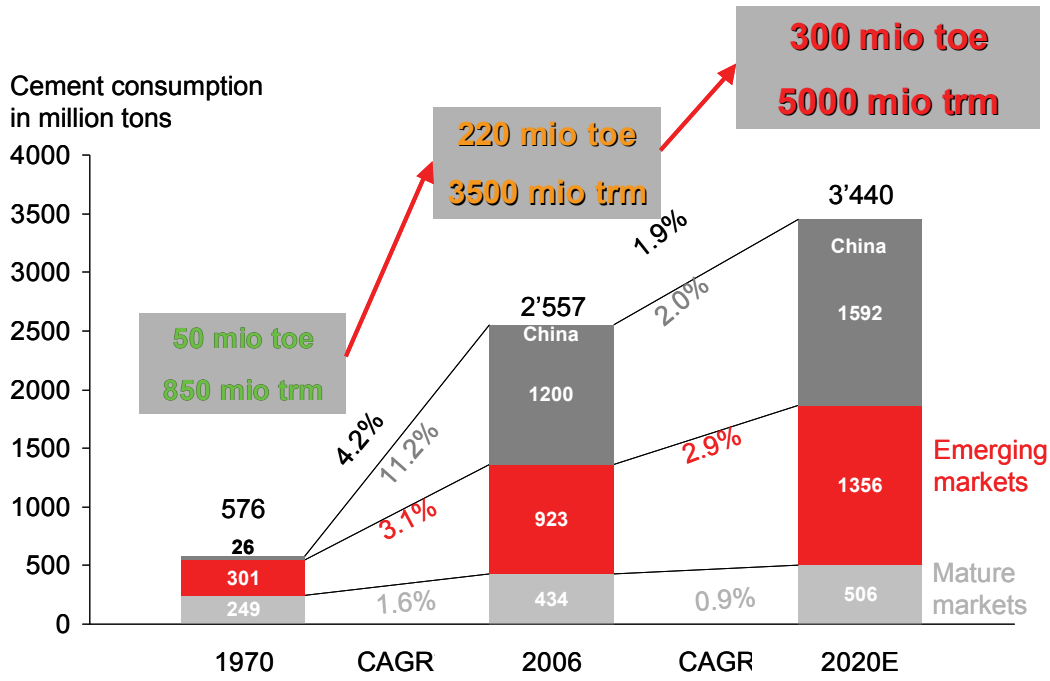
2. Cement manufacture is a resource intensive industry. Normally about 1,5 to 1,7 tonnes of raw materials are quarried per tonne of clinker produced. In addition, the manufacturing process of clinker requires substantial energy in order to bring the kilns to temperatures of over 2000 °C. According to Cembureau, the representative organization of the cement industry in Europe, each tonne of cement produced typically requires 60 to 130 kilograms of fuel oil or its equivalent, depending on the cement type and kiln technology employed, and about 105 KWh of electricity (Loréa, 2007). On average, energy costs (in the form of fuel and electricity) represent 40 percent of cement manufacturing costs (European IPPC Bureau, 2009).

3. In 2008, global cement production was estimated to be 2.9 billion tonnes, with China responsible for about half of the world's production (Da Hai et al., 2009; U.S. Geological Survey, 2009). Consumption of cement is driven primarily by activity in the construction industry, and so is closely linked to the economic cycle. World cement consumption could reach 3,4 billion tonnes by 2020 (Figure 1), with the corresponding increases in energy and raw materials needs.

4. The cement industry has undergone significant consolidation over the past decade through mergers and acquisitions, becoming increasingly characterised by the presence of large, multinational firms. This notwithstanding, it remains a sector with a fairly low global market concentration with the five largest companies accounting for less than 20% of global output[1].

[1] According to data obtained from company annual reports: Lafarge (France), Holcim (Switzerland), Cemex (Mexico), Anhui Conch (China), HeidelbergCement (Germany).

Figure 1. Estimated world demand of cement



toe = tons of oil equivalent (42 GJ) ; trm = tons of raw material ; CAGR = Compound annual growth rate

Source: Degré (2009)

5. The clinker burning process is the most important part of the production process in terms of the key environmental issues associated with cement manufacture: energy use and emissions to air. Depending on the specific production processes, cement plants cause emissions to air and waste emissions to land (including cement kiln dust, CKD, where recycling back into the production process may be restricted). In specific rare cases, emissions to water may occur. Additionally, the environment can be affected by noise and odours. The key pollutants released to air are particulates, nitrogen oxides (NO_X) and sulphur dioxide (SO_2) (European IPPC Bureau, 2009). Carbon oxides (CO, CO_2), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCCDs/PCDFs), volatile organic compounds (VOC), metals and their compounds, hydrogen chloride (HCl) and hydrogen fluoride (HF) are emitted as well. Worldwide, cement making is thought to account for 6 percent of the total carbon dioxide (CO_2) emissions from stationary sources (IPCC, 2005). The type and quantity of air emissions depend on different parameters, for example, inputs (the raw materials and fuels used) and the type of process applied. Cement industry operations are also associated with impacts of resource extraction (fossil fuel, limestone, and other minerals) upon environmental quality, biodiversity, and landscape aesthetics; and depletion of non-renewable or slowly renewable resources (fossil fuels or groundwater) (Battelle, 2002).

1.2. Co-processing of Hazardous Waste in the Cement Industry

6. Co-processing in resource-intensive industries (RII) involves the use of waste materials in manufacturing processes for the purpose of energy and/or resource recovery and resultant reduction in the use of conventional fuels and/or raw materials through substitution. In particular, the co-processing of waste materials in cement kilns, the subject of these guidelines, allows the recovery of the energy or mineral value from waste materials, while cement is being produced.

7. Co-processing is a sustainable development concept based on the principles of industrial ecology (Mutz et al., 2007; Karstensen, 2009a), a discipline that focuses on the potential role of industry in reducing environmental burdens throughout the product life-cycle. One of the most important goals of industrial ecology is to make one industry's waste another's raw material (OECD, 2000). Within the cement industry, the use of wastes as fuel and/or raw materials is an example of this type of exchange.

8. In co-processing, wastes serve a useful purpose in replacing part of the materials which would have had to be used for fuel and/or raw materials, thereby conserving natural resources; as such, under the Basel Convention co-processing constitutes an operation "which may lead to resource recovery[2], recycling, reclamation, direct reuse or alternative uses" under R1 ("use as a fuel or other means to generate energy") and/or R5 ("recycling/reclamation of other inorganic materials") of Annex IVB to the Convention.

9. The Basel Convention places obligations on countries that are Parties to ensure environmentally sound management (ESM) of hazardous and other wastes. In this regard, the guiding principle broadly accepted for securing a more sustainable waste management system is the waste hierarchy of management practices which places waste prevention (avoidance) and recovery in a preeminent position relative to disposal. Where waste avoidance is not possible, reuse, recycling and recovery becomes, in many cases, a preferable alternative to final disposal. To this end, co-processing in cement kilns provides an environmentally sound resource recovery option for the management of wastes, preferable to landfilling and incineration.

10. Fossil fuels and raw materials have been successfully substituted by different types of wastes in cement kilns in Europe, Japan, United States, Canada and Australia since the beginning of the 1970s (GTZ/Holcim, 2006). The experience of various jurisdictions with the use of wastes as fuels and/or raw materials in cement kilns is reviewed by CCME (1996), EA (1999a), Twigger et al. (2001) and Karstensen (2007a), among others.

11. Although the practice varies among individual plants, cement manufacture can consume significant quantities of wastes as fuel and non-fuel raw materials. This consumption reflects the process characteristics in clinker kilns, that ensures the complete breakdown of the raw materials into their component oxides and the recombination of the oxides into the clinker minerals. The essential process characteristics for the use of waste can be summarised as follows (European IPPC Bureau, 2009):

- Maximum temperatures of approximately 2000°C (main firing system, flame temperature) in rotary kilns;
- Gas retention times of about 8 seconds at temperatures above 1200°C in rotary kilns;
- Material temperatures of about 1450°C in the sintering zone of rotary kilns;
- Oxidising gas atmosphere in rotary kilns;
- Gas retention time in the secondary firing system of more than 2 seconds at temperatures above 850°C; in the precalciner, the retention times are correspondingly longer and temperatures are higher;

[2] In accordance with the European Court of Justice's judgement of 13 February 2003 delivered in case C-458/00.

- Solids temperatures of 850°C in the secondary firing system and/or the calciner;
- Uniform burnout conditions for load fluctuations due to the high temperatures at sufficiently long retention times;
- Destruction of organic pollutants due to the high temperatures at sufficiently long retention times;
- Sorption of gaseous components like HF, HCl, and SO_2 on alkaline reactants;
- High retention capacity for particle-bound heavy metals;
- Short retention times of exhaust gases in the temperature range known to lead to formation of PCDDs/PCDFs;
- Complete utilisation of fuel ashes as clinker components and hence, simultaneous material recycling and energy recovery;
- Product specific wastes are not generated due to a complete material utilisation into the clinker matrix (although some cement plants dispose of CKD or bypass dust);
- Chemical-mineralogical incorporation of non-volatile heavy metals into the clinker matrix.

12. As highlighted by various authors (for example, Mantus, 1992; Battelle, 2002; WBCSD, 2005; Karstensen, 2007b), the utilisation of wastes in the cement industry, principally as alternative fuels but also as supplementary raw materials, has numerous potential benefits, including the recovery of the energy content of waste, conservation of non-renewable fossil fuels, reduction of CO_2 emissions, reduction in production costs, and use of an existing technology to treat hazardous wastes.

13. The embodied energy in alternative fuels that is harnessed by cement plants is the most direct benefit, as it replaces demand for fossil fuels (Murray and Price, 2008). By co-processing waste in a cement kiln and substituting for a non-renewable source, fossil fuel dependency is reduced and savings are made through resource conservation. The amount of fossil fuel demand that is displaced depends, among other factors, on the calorific value and water content of the alternative fuel.

14. Additionally, the fuel substitutes may have lower carbon contents (on a mass basis) than fossil fuels, and alternative raw materials such as slags or fly ash, that do not require significantly more heat (and hence fuel) to process, may contribute part of the CaO needed to make clinker from a source other than $CaCO_3$ (Van Oss, 2005). Therefore, another direct benefit of waste co-processing is a potential reduction in CO_2 emissions from cement manufacturing. Moreover, through integrating cement kilns within an overall waste management strategy, co-processing may offer a potential to reduce net global CO_2 emissions relative to a scenario in which waste is combusted in an incinerator without energy recovery (EA, 1999b; Cembureau, 2009).

15. The use of alternative materials to replace the traditional raw materials also reduces the exploitation of natural resources and the environmental footprint of such activities (WBCSD, 2005; Cembureau, 2009).

16. In addition to the aforementioned direct advantages of using waste materials for cement manufacturing, there are cost savings derived from the utilisation of pre-existing kiln infrastructure to co-process waste that cannot be minimised or otherwise recycled, thus avoiding the need to invest in purpose-built incinerators or landfill facilities (GTZ/Holcim, 2006; Murray and Price, 2008). Furthermore, unlike with dedicated waste incinerators, when waste materials are co-

processed in cement kilns, ash residues are incorporated into the clinker, so there are no end-products that require further management.

17. The above notwithstanding, co-processing of hazardous waste in cement kilns should only be performed if the kiln operates according to the best available techniques, and if certain requirements with respect to input control, process control and emission control are met (as described in later sections of these guidelines). Moreover, an appropriate national legal and regulatory framework within which hazardous waste management activities can be planned and safely carried out should be in place to ensure that the waste is properly handled from the point of generation until its disposal, through the operations of segregation, collection, storage, and transportation. Parties to the Basel and Stockholm Conventions should also examine national controls, standards and procedures to ensure that they are in agreement with the conventions and with their obligations under them, including those which pertain to the ESM of hazardous wastes.

2.Key Aspects in Co-processing of Hazardous Waste in Cement Kilns

2.1. Principles of Co-processing in the Cement Industry

18. Waste co-processing in cement manufacturing, when carried out in a safe and sound manner, is recognised for far-reaching environmental benefits (Cembureau, 1999a; 2009), however these may be outweighed by poor planning if, for instance, it results in increased pollutant emissions or fails to give priority to a more desirable waste management practice (in terms of the overall environmental outcome). A set of general principles were developed by Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH and Holcim Group Support Ltd. to help avoid the latter scenarios (GTZ/Holcim, 2006). These principles (Table 1) provide a comprehensive yet concise summary of the key considerations for co-processing project planners and stakeholders. Similar principles have also been outlined by the World Business Council for Sustainable Development (WBCSD, 2005) and Karstensen (2009a) (see Table 2).

Table 1. General principles for co-processing of wastes in cement kilns

Principle	Description
The waste management hierarchy should be respected	– Waste should be co-processed in cement kilns only if there are not more ecologically and economically better ways of recovery – Co-processing should be considered an integrated part of waste management – Co-processing should be in line with the Basel and Stockholm Conventions and other relevant international environmental agreements
Additional emissions and negative impacts on human health must be avoided	– Negative effects of pollution on the environment and human health must be prevented or kept at a minimum – Air emissions from cement kilns co-processing waste cannot be statistically higher than those not co-processing waste
The quality of the cement must remain unchanged	– The product (clinker, cement, concrete) must not be used as a sink for heavy metals – The product must not have any negative impacts on the environment (for example, as determined by leaching tests) – The quality of the product must allow for end-of-life recovery
Companies that co-process must be qualified	– Assure compliance with all laws and regulations – Have good environmental and safety compliance records – Have personnel, processes, and systems in place committed to protecting the environment, health, and safety – Be capable of controlling inputs to the production process – Maintain good relations with public and other actors in local, national and international waste management schemes
Implementation of co-processing must consider national circumstances	– Country specific requirements and needs must be reflected in regulations and procedures – A stepwise implementation allows for the build-up of required capacity and the set-up of institutional arrangements – Introduction of co-processing goes along with other change processes in the waste management sector of a country

Source: GTZ/Holcim (2006)

Table 2. General requirements for co-processing of hazardous wastes in cement kilns

(1)	An approved environmental impact assessment (EIA) and all necessary national/local permits;
(2)	Compliance with all relevant national and local regulations;
(3)	Compliance with the Basel and the Stockholm Conventions;
(4)	Approved location, technical infrastructure and processing equipment;
(5)	Reliable and adequate power and water supply;
(6)	Adequate air pollution control devices and continuous emission monitoring ensuring compliance with regulation and permits; needs to be verified through regular baseline monitoring;
(7)	Exit gas conditioning/cooling and low temperatures (< 2000°C) in the air pollution control device to prevent dioxin formation;
(8)	Clear management and organisational structure with unambiguous responsibilities, reporting lines and feedback mechanism;
(9)	An error reporting system for employees;
(10)	Qualified and skilled employees to manage hazardous wastes and health, safety and environmental issues;
(11)	Adequate emergency and safety equipment and procedures, and regular training;
(12)	Authorised and licensed collection, transport and handling of hazardous wastes;
(13)	Safe and sound receiving, storage, preparation and feeding of hazardous wastes;
(14)	Adequate laboratory facilities and equipment for hazardous waste acceptance and feeding control;
(15)	Demonstration of hazardous waste destruction performance through test burns;
(16)	Adequate record keeping of hazardous wastes and emissions;
(17)	Adequate product quality control routines;
(18)	An environmental management and continuous improvement system certified according to ISO 14001, EMAS or similar;
(19)	Regular independent audits, emission monitoring and reporting;
(20)	Regular stakeholder dialogues with local community and authorities, and for responding to comments and complaints;
(21)	Open disclosure of performance reports on a regular basis.

Source: Karstensen (2009a)

2.2. Considerations for Selection of Wastes

19. The strict quality controls for cement products and the nature of the manufacturing process mean that only carefully selected waste is suitable for use in co-processing (WBCSD, 2005). Moreover, changes in technology and consumer behaviour mean that co-processing may not always be the most cost-effective or environmentally preferred way of using a waste stream. Such decisions may need to be re-evaluated over time.

20. When deciding on the suitability of a waste stream for co-processing, besides taking into consideration the chemical composition of the final product (cement) and determining whether the use of the waste will result in damage to the environment or public health and safety, it needs to be ascertained that cost-effective higher-order uses of the material, according to the waste management hierarchy, are not available. Life Cycle Assessment (LCA) is a tool that may assist the decision making process by comparing different waste management scenarios.

21. As a basic rule, waste accepted as an alternative fuel and/or raw material should give an added value for the cement kiln in terms of the heating value of the organic part and/or the material value of the mineral part. As the operating characteristics of cement plants are variable, the precise composition of the wastes will be dependent upon each plant's ability to handle any particular waste stream. Even so, wastes with a low heating value and very high heavy metal content will generally not be suitable for co-processing in a cement kiln. The use of cement kilns as a disposal operation not leading to resource recovery, should only be considered as a means to solve a local waste management problem if there are no other adequate treatment facilities in the country and if such undertaking does not negatively impact the environment, public health, or product quality.

22. Due to the heterogeneous nature of waste, blending and mixing of different waste streams may be required to guarantee a homogeneous feedstock that meets specifications for use in a cement kiln. However, blending of hazardous wastes should not be conducted with the aim to lower the concentration of hazardous constituents in order to circumvent regulatory requirements. As a general principle, the mixing of wastes must be prevented from leading to the application of an unsuitable (non-environmentally sound) disposal operation (European IPPC Bureau, 2006).

2.2.1 Hazardous wastes suitable for co-processing in cement kilns

23. A wide range of wastes are amenable to co-processing; however, because cement kiln emissions are site-specific, the decision on what type of waste can be finally used in a certain plant cannot be answered uniformly. The selection of wastes is influenced by many factors other than the nature of the waste itself. Consideration needs to be given to kiln operation; raw material and fuel compositions; waste feed points; gas-cleaning process; resulting clinker quality; general environmental impacts; probability of formation and release of persistent organic pollutants (POPs); particular waste management problems; regulatory compliance; and public and government acceptance (Van Oss and Padovani, 2003; GTZ/Holcim, 2006; UNEP, 2007; European IPPC Bureau, 2009).

24. The operator should develop a waste evaluation procedure to assess potential impacts on the health and safety of workers and the public, plant emissions, operations and product quality. Some of the variables that should be considered when selecting waste materials include (WBCSD, 2005; UNEP, 2007):

(a) Kiln operation:

- Alkali (sodium, potassium, etc.), sulphur and/or chloride content: Excessive inputs of alkalis, sulphur and/or chlorides may lead to 'build-up' and blockages in the kiln system. Where these compounds cannot be further captured in the cement clinker or kiln dust, a bypass may be required to remove excess alkali, chloride and sulphur compounds from preheater/precalciner kiln systems. In addition, high alkali content may limit recycling of CKD to the operation.
- Heating (calorific) value: The heating value is the key parameter for the energy provided to the process.
- Water content: High water content may reduce the productivity and efficiency of the kiln system.
- Ash content: The ash content affects the chemical composition of the cement and may require an adjustment of the composition of the raw mix.

- Exhaust gas flow rate and waste feed rate, to assure sufficient residence time for destruction of organics and to prevent incomplete combustion due to waste overcharging.

- Stability of operation (for example, duration and frequency of CO trips), and the state (liquid, solid), preparation (shredded, milled) and homogeneity of the waste.

(b) Emissions:

- Sulphur content: Sulphur bearing waste may result in the release of sulphur oxides.

- Organic content: Organic constituents may result in emissions of CO_2, CO and other products of incomplete combustion (PICs).

- Chloride content: These may combine with alkalis to form fine particulate matter composed of chlorides of those alkalis, which can be difficult to control; in some cases, chlorides have combined with ammonia present in the limestone feed to produce highly visible detached plumes of fine particulate composed mainly of ammonium chloride.

- Metals content: The non-volatile behaviour of the majority of heavy metals means that most pass straight through the kiln system and leave as a constituent of the clinker. Volatile metals introduced into the kiln will be in part internally recycled by evaporation and condensation processes, if not emitted in the exhaust gas of the kiln, and build-up within the kiln system until equilibrium is reached and maintained. Thallium, mercury and their compounds are easily volatilized and to a lesser extent so are cadmium, lead, selenium and their compounds. Dust control devices can only capture the particle-bound fraction of heavy metals, which needs to be taken into account when wastes containing volatile metals are co-processed. Wood treated with copper, chromium, arsenic etc. also requires special consideration with regard to the efficiency of the exhaust gas cleaning system. Mercury is a highly volatile metal that is difficult to capture in air pollution control equipment, so the amount of mercury in the total waste feed to kilns should be limited.

- Alkali bypass exhaust gas: At facilities equipped with an alkali bypass, the alkali bypass gases can be released either from a separate exhaust stack or from the main kiln stack. The pollutants in this gas stream are similar to those in the main kiln exhaust gases and similar pollution abatement equipment and monitoring is required.

(c) Clinker, cement and final product quality:

- Phosphate content: Phosphates retard setting time.

- Fluorine content: Elevated levels of fluorine affect setting time and strength development.

- Chlorine, sulphur, and alkali content: These affect overall product quality.

- Thallium and chromium content: These affect cement quality and may cause allergic reactions in sensitive users. The leachability of chromium from concrete debris may be higher than that of other metals (Van der Sloot et al., 2008).

- Leachable trace elements: Under stagnant water conditions, leaching rates of aluminium from cementitious materials can exceed drinking water limits (Van der Sloot et al., 2008).

25. Generally, only sorted waste with a known composition and known energy and/or mineral value is suitable for co-processing in cement kilns. Moreover, plant-specific health and safety concerns need to be addressed as well as due consideration given to the waste management

hierarchy (as a general principle). Consequently, the following wastes are normally not recommended for co-processing in cement kilns:

- Radioactive waste;
- Electric and electronic waste (e-waste);
- Whole batteries;
- Corrosive waste;
- Reactive waste, including explosive waste, cyanide bearing waste and water-reactive waste;
- Mercury waste; and
- Waste of unknown or unpredictable composition, including unsorted municipal waste.

26. Individual facilities may exclude other wastes outside the above list depending on local circumstances. For instance, lack of regulations – and enforcement – governing health care waste management, particularly segregation at the source, will likely cause some facilities to not accept this type of waste based on health and safety concerns, although process conditions in cement kilns would be appropriate to dispose of infectious wastes.

27. Besides health and safety concerns, wastes that are not recommended for co-processing in cement kilns are in general excluded from consideration because of their potentially negative impacts on kiln operation, clinker quality and air emissions, and when an alternative waste management option should be preferred.

28. Cement plants are not designed or operated to meet safety and health requirements for radioactive waste management, for which the preferred approach is concentration (reduction of volume) and containment of radionuclides by means of a conditioning process to prevent or substantially reduce dispersion in the environment.

29. Electric and electronic waste contains valuable resources such as precious metals and recycling should be the preferred option. Co-processing of the plastic parts of electronic waste might be an option, but this requires disassembling and segregation first.

30. Co-processing of batteries would lead to undesirable concentrations of pollutants in the cement and air emissions. Moreover, there are commercially viable battery recycling plants that should be the preferred waste management option.

31. Chlorine and sulphur contents of mineral acids have a negative impact on the clinker production process, affecting product quality and possibly leading to unwanted gaseous emissions. Acids may also corrode and damage the production facilities.

32. Explosive waste should not be co-processed because explosive reactions in the cement kiln would have a negative impact on process stability. There are also occupational safety concerns due to the risk of uncontrolled explosions during transport and pre-processing activities.

33. The high volatility of mercury in cement kilns poses a problem regarding air emissions. It is generally recommended that wastes that contain more than 10 ppm mercury should not be fed to the kiln.

2.2.2 Waste recovery and final disposal in cement kilns

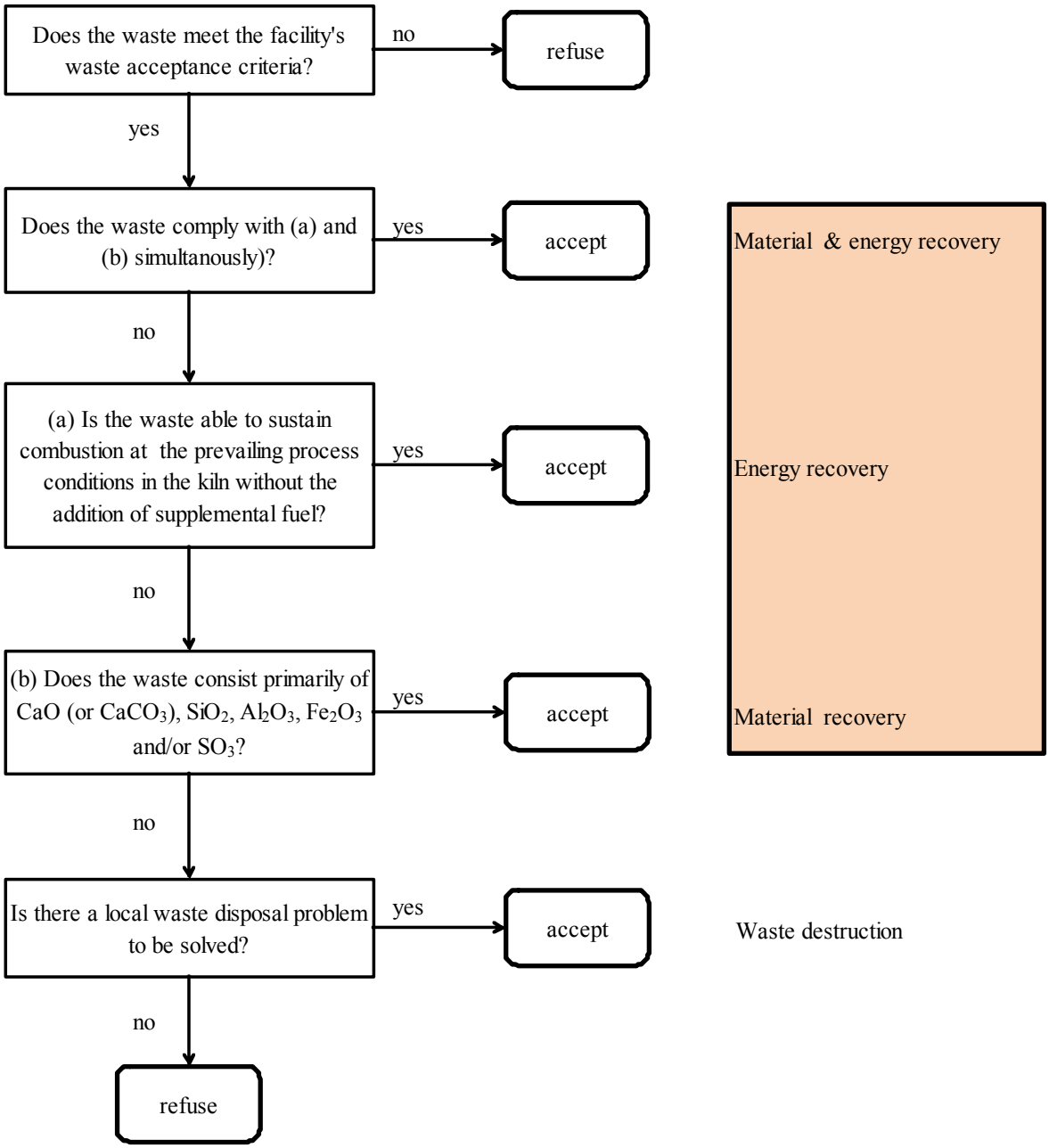
34. Selected waste streams with recoverable energy value can be used as fuels in a cement kiln, replacing a portion of conventional fuels, if they meet specifications. Similarly, selected waste streams containing useful minerals such as calcium, silica, alumina, and iron can be used as raw materials in the kiln, replacing raw materials such as clay, shale, and limestone. Some wastes will meet both of these requirements and will be suitable for processing for energy recovery and for materials recovery or as an ingredient.

35. Conversely, waste combustion in a cement kiln without any substitution, and solely for the purpose of destruction, should be considered to constitute disposal by thermal treatment.

36. To distinguish between operations that lead to resource recovery and those that do not, specific criteria may need to be developed to evaluate the contribution of the waste to the production process. The general decision-making process is outlined in Figure 2. To this respect, some approaches have been proposed that consider, for example, either the higher or the lower heating value of the waste to assess its energy value, and the material's chemical composition (ash, CaO or $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, SO_3, and/or water) to assess its mineral value (Zeevalkink, 1997; Koppejan and Zeevalkink, 2002; GTZ/Holcim, 2006). An example is provided in Annex 2.

37. Although wastes with little or no energy or mineral value should not be considered for co-processing, the high temperatures, long residence times, and oxidizing conditions provided by cement kilns, make it possible, at the request of national or local governments, for the kilns to be used for the disposal of particularly problematic waste streams such as obsolete pesticide stocks. However, this is an activity that is outside the scope of co-processing, and needs to be assessed on a case-by-case basis as well as agreed upon jointly by regulatory authorities and operators. Trial burns may need to be conducted to demonstrate that performance criteria are met.

Figure 2. Waste acceptance decision process



2.2.3 Trial burns

38. To verify the ability of a facility to efficiently destroy organic components found in hazardous wastes in an irreversible and sound way, the destruction and removal efficiency (DRE) or destruction efficiency (DE) should be determined, as demonstrated in a trial burn. The trial burn involves selecting a principal organic hazardous constituent (POHC) in the waste feed, and sampling and analysis to determine input and emission rates of the same POHC. A trial burn typically consists of a series of tests (one for each set of operating conditions for which the facility desires to be permitted), and there are usually three runs performed for each test.

39. Trial burns with hazardous wastes require professional supervision and independent verification (Karstensen, 2008a). Prior to a trial burn, the operator should demonstrate to the satisfaction of the competent authorities that the baseline operation is properly controlled and that there are safeguards against potential environmentally damaging abnormal operations.

40. During the trial burn, operating limits are established for parameters that may adversely affect the attainment of the demonstrated DRE or DE during routine operations: namely, maximum hazardous waste feed and maximum kiln production rate (Karstensen, 2009b). Subsequent to the trial burn, permit limits are established for these parameters.

41. Trial burns are recommended to demonstrate destruction of wastes consisting of, containing or contaminated with POPs. A cement kiln should demonstrate that it is capable of destroying (through combustion) or removing (through settling in ductwork or capture in air pollution control devices) at least 99.9999 percent of targeted POPs (for non-POPs contaminants a DRE of 99.99 percent needs to be demonstrated). Moreover, a PCDDs/PCDFs emission limit of 0.1 ng TEQ/Nm^3 [3] should be met under testing conditions (SBC, 2007). The cement kiln should also comply with existing emission limit values.

42. An alternative approach to trial burns under worst-case conditions, that is considered to provide the same qualitative information, has been proposed by Karstensen (2009b). This involves conducting a baseline emissions study (no hazardous waste fed to the kiln) and one test run to obtain destruction performance and pollutant emissions data while feeding hazardous waste into the kiln; both tests conducted under normal operating conditions, all the while meeting an emissions limit for PCDDs/PCDFs of 0.1 ng TEQ/Nm^3 as well as meeting other regulatory requirements. This approach for performance verification, together with adequate safety arrangements, input control and operational procedures, is thought to secure the same level of environmental protection as current regulation in the European Union (GTZ/Holcim, 2006). This approach was used to demonstrate a DRE of 99.9999969 percent for fenobucarb and 99.9999832 percent for fipronil in a cement kiln in Vietnam (Karstensen et al., 2006).

43. A compilation of performance verification and test burns results are provided in Annex 3.

2.3. Quality Assurance/Quality Control

44. A comprehensive quality assurance (QA) and quality control (QC) programme is necessary to ensure that the product meets standard specifications, that plant operations are not negatively affected by the use of hazardous wastes, to protect the environment and to reduce risks to worker health and safety. QA is necessary for ensuring that all data and the decisions based on that data are technically sound, statistically valid, and properly documented.

45. A QA plan should be prepared to help ensure that the monitoring, sampling, and analytical data meet specific objectives for precision, accuracy, and completeness, and to provide the framework for evaluating data quality. The plan should encompass all materials handled at the facility (waste streams and product), and should give detailed instructions for the following:

- Organization and responsibilities;

[3] Dry basis, corrected to 11 percent O_2, 101.3 kPa and 273.15 K.

- QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability;
- Sampling procedures;
- Sample handling and custody;
- Analytical procedures;
- QC checks (blanks, spikes, replicates, etc.) and frequency;
- Instrument/equipment testing, inspection, or maintenance;
- Instrument/equipment calibration procedures and frequency; and
- Data review, verification, validation, and reporting.

46. Adequate laboratory design, infrastructure, equipment, and instrumentation should be provided and maintained to ensure that all required analysis are completed in a timely manner. Periodic interlaboratory tests should be considered in order to evaluate and improve laboratory performance.

47. Safety and health considerations should be taken into consideration when conducting sampling. Employees who perform sampling activities should be properly trained with respect to the hazards associated with waste materials, as well as with any waste handling procedures that will assist in protecting the health and safety of the sampler. In addition, the employees should be trained in the proper protective clothing and equipment that must be used when performing sampling activities. All persons involved in sampling activities should be fully aware of applicable QA/QC procedures.

48. As regards best available techniques (BAT) for waste quality control in the cement industry, the following have been identified by the European IPPC Bureau (2009):

- To apply QA systems to guarantee the characteristics of wastes and to analyse any waste that is to be used as raw material and/or fuel in a cement kiln for: constant quality; physical criteria, for example, emissions formation, coarseness, reactivity, burnability, calorific value; chemical criteria, for example, chlorine, sulphur, alkali and phosphate content and relevant metals content;
- To control the amount of relevant parameters for any waste that is to be used as raw material and/or fuel in a cement kiln, such as chlorine, relevant metals (for example, cadmium, mercury, thallium), sulphur, total halogen content; and
- To apply QA systems for each waste load.

49. Internal audits should be carried out with sufficient frequency to ensure that QA/QC procedures are in use and to ensure that personnel conform to these procedures. Independent third party audits should be conducted at least once a year. Audit reports should be submitted to management with requirements for a plan to correct observed deficiencies.

2.4. Health and Safety Aspects

50. The protection of health and safety during hazardous waste activities should be integrated into all aspects of facility operations, and should be a conscious priority for all involved, from

corporate management to the most recently hired employee. Overall and specific personnel requirements, the chain of command, and individual roles and responsibilities, should be clearly established.

51. A health and safety programme should be designed to identify, evaluate, and control safety and health hazards, and provide for emergency response for hazardous waste operations. The content and extent of this programme should be proportionate to the types and degrees of hazards and risks associated with specific operations.

52. Adequate documentation and information on safe hazardous waste handling, operating procedures and emergency contingency measures are mandatory. Facility management staff must ensure an informed workforce through openness and transparency about health and safety measures and standards. Safety and emergency instructions must be provided to employees and contractors in due time, and should be easily understandable.

2.4.1 Hazard analysis

53. The hazards and potential exposures affecting facility employees should be determined to ensure that appropriate control practices and techniques are in place to maintain worker health and safety, and identify hazards present that would require the use of personal protective equipment (PPE). To this end, techniques such as job hazard analysis (JHA), job safety analysis (JSA), safety analysis reports (SAR), process hazard analysis (PHA), and job, task, and hazard analysis (JTHA), are recommended.

2.4.2 Access and hazard control

54. To eliminate or control worker exposure to hazards, the following should be considered (in order of preference):

- Engineering controls, to preclude worker exposure by removing or isolating the hazard (for example, ventilation or use of remotely operated material handling equipment);
- Administrative controls, to manage worker access to hazards or establish safe work procedures (for example, security measures to prevent unauthorized or unprotected access to hazardous wastes on-site); and
- PEE, when engineering or administrative controls are not feasible or do not totally eliminate the hazard.

55. An appropriate combination of the above should be used to reduce and maintain employee exposure to or below published exposure levels, examples of which include: the Threshold Limit Value (TLV) occupational exposure guidelines published by American Conference of Governmental Industrial Hygienists (ACGIH); the Pocket Guide to Chemical Hazards published by the United States National Institute for Occupational Health and Safety (NIOSH); Permissible Exposure Limits (PELs) published by the Occupational Safety and Health Administration of the United States (OSHA); Indicative Occupational Exposure Limit Values (IOELVs) published by European Union member states, or other similar sources.

56. For hazardous substances and health hazards for which there is no permissible exposure limit or published exposure limit, the operator should use the published literature and material safety data sheets (MSDS) as a guide in making the determination as to what level of protection is appropriate.

2.4.3 Personal protective equipment

57. Employees, contractors and individuals visiting the installation, should be provided with and required to use PPE where engineering control methods are infeasible to reduce exposure to or below the permissible exposure limits. PEE should be selected to protect against any hazard that is present or likely to be present and should be appropriate to the task-specific conditions and duration.

58. An explanation of equipment selection and use, maintenance and storage, decontamination and disposal, training and proper fit, donning and doffing procedures, inspection, in-use monitoring, program evaluation, and equipment limitations, should be provided to all personnel involved in hazardous waste operations.

2.4.4 Training

59. Effective training is one of the most important keys to worker safety and health. Employees should be trained to a level required by their job function and responsibility before they are permitted to engage in hazardous waste operations that could expose them to hazardous substances, safety, or health hazards. Training activities should be adequately monitored and documented (curriculum, duration, and participants).

60. The training should cover safety, health and other hazards present on the facility; use of personal protective equipment; work practices by which the employee can minimize risks from hazards; safe use of engineering controls and equipment on the site; and, medical surveillance requirements including recognition of symptoms and signs which might indicate over exposure to hazards. Employees who are engaged in responding to hazardous emergency situations should also be trained in how to respond to such expected emergencies.

2.4.5 Medical surveillance

61. A medical monitoring programme should be implemented to assess and monitor employee health and fitness both prior to employment and during the course of work, to provide emergency and other treatment as needed. An effective programme should consider at least the following components:

- Pre-employment screening, to determine physical fitness, including the ability to work while wearing PPE, and provide baseline data for future exposures;
- Periodic medical monitoring examinations (the content and frequency of which would depend on the nature of the work and exposure), to determine biological trends that may mark early signs of chronic adverse health effects; and
- Provisions for emergency treatment and acute non-emergency treatment.

2.4.6 Emergency response

62. Emergency preparedness should be established for the protection of the workforce and public before hazardous waste operations can begin. An Emergency Response Plan should be in place to ensure that appropriate measures are taken to handle possible on-site emergencies and coordinate off-site response. At minimum, this plan should address the following:

- Pre-emergency planning and coordination with outside emergency responders;

- Personnel roles, lines of authority, training and communication procedures;
- Emergency recognition and prevention procedures;
- Safe distances and places of refuge;
- Site security and control procedures;
- Evacuation routes and procedures;
- Site mapping highlighting hazardous areas, site terrain, site accessibility and off-site populations or environments at potential risk;
- Decontamination procedures;
- Emergency medical treatment and first aid procedures;
- Personal protective and emergency equipment at the facility;
- Emergency alerting and response procedures;
- Documenting and reporting to local authorities; and
- Critique of response and follow-up procedures.

63. Emergency equipment, such as fire extinguishers, self-contained breathing apparatus, sorbents and spill kits, and shower/eye wash stations should be located in the immediate vicinity of the hazardous waste storage and processing areas.

64. The Plan requirements should be rehearsed regularly using drills and mock situations, and reviewed periodically in response to new or changing facility conditions or information.

65. Arrangements should be made to familiarize local authorities and emergency responders with the layout of the facility; properties of hazardous waste handled at the facility and associated hazards; places where facility personnel would normally be working; facility entrances and possible evacuation routes. Arrangements agreed to by local authorities, hospitals and emergency response teams should be described in the Emergency Response Plan.

2.5. Communications and Stakeholder Involvement

66. Stakeholders are all the individuals and groups who see themselves as potentially affected by the operations of a facility, whether on a local, national, or international scale. These include, but are not limited to, neighbours, community organizations, employees, trade unions, government agencies, the media, non-governmental organizations (NGOs), contractors, suppliers, and investors.

67. Public communication means providing information through any media, including brochures, websites, newspapers, radio and television. Stakeholder involvement means listening directly to community members and others with an interest in the facility, through public meetings, presentations, advisory committees, and personal conversations.

68. Communication and stakeholder involvement should occur as part of the normal operations of a plant. Facilities need to be clear about their objectives for working with stakeholders, have a reasonable timescale for engagement, commit the necessary resources, and be prepared to work with stakeholders to find mutually beneficial outcomes. Detail on how to design and develop a

communications and stakeholder involvement plan is provided by U.S. EPA (1996), Hund et al. (2002), and The Environment Council (2007), among others.

69. Operators and regulatory authorities should be prepared to address public concerns over possible impacts of co-processing, and they should strive to establish efficient communication processes in order to explain the activities. Operators planning to handle and/or co-process hazardous waste should provide all necessary information to allow stakeholders to understand the purpose of the use of such wastes in the cement kiln, and to make them aware of the measures that will be implemented to avoid adverse impacts on the public and the environment.

3.Waste Acceptance and Pre-processing

3.1. Introduction

70. Co-processing in cement kilns generally requires some degree of waste processing to produce a relatively uniform waste stream that complies with the technical and administrative requirements of cement manufacture and to guarantee that environmental standards are met. Only in few instances, such as used oil or tyres, wastes can be used 'as-delivered' and without further processing.

71. With any process, the quality of what goes in determines the quality of what comes out. Therefore, attention should be paid to the selection of suitable waste materials, whether they are collected directly from the generators or through intermediaries. Operators need to ensure that only hazardous waste originating from trustworthy parties will be accepted (with deliveries of unsuitable wastes refused), considering the integrity of all participants throughout the supply chain. Only qualified, authorized and licensed transport companies should be used, otherwise, serious accidents and incidents may arise due to incompatible, poorly labelled or poorly characterised wastes being mixed or stored together.

3.2. Waste Acceptance

72. Knowledge of wastes, before they are accepted and processed, is necessary to enable the operator to ensure that the waste is within the requirements of the facility's permit and will not adversely affect the process.

73. Waste acceptance comprises two stages: pre-acceptance (or screening) and on-site acceptance. Pre-acceptance should involve the provision of information and representative samples of the waste to allow operators to determine the suitability of the waste before arrangements are in place to accept the waste. The second stage should involve acceptance procedures when the waste arrives at the facility to confirm the characteristics of waste previously approved.

74. Failure to adequately screen waste samples prior to acceptance and to confirm its composition on arrival at the installation may lead to subsequent problems, including an inappropriate storage and mixing of incompatible substances, and accumulation of wastes.

3.2.1 Pre-acceptance

75. A pre-acceptance (or pre-shipment screening) protocol should be designed to ensure that only hazardous waste streams that can be properly and safely handled are approved for shipment to the facility. Such protocol is necessary to:

- Ensure regulatory compliance by screening out unsuitable wastes;
- Confirm the details relating to composition, and identify verification parameters that can be used to test waste arriving at the facility;
- Identify any substances within the waste that may affect its processing, or react with other reagents; and
- Accurately define the range of hazards exhibited by the waste.

76. The operator should obtain information on the nature of the process producing the waste, including the variability of this process; an appropriate description of the waste regarding its composition (chemicals present and individual concentrations), handling requirements and associated hazards; the quantity of waste; the form the waste takes (solid, liquid, sludge etc); and, sample storage and preservation techniques. Where possible, the information should be provided by waste generators themselves, otherwise a system for the verification of the information provided by any intermediaries should be considered.

77. A system for the provision and analysis of a representative sample(s) of the waste should be in place. The waste sample should be taken by a person who is technically competent to undertake the sampling process, and analysis should be carried out by a laboratory (preferably accredited) with robust QA/QC methods and record keeping; a chain-of-custody procedure should be considered. The operator should ensure that, for each new waste, a comprehensive characterisation (profiling) and testing with respect to the planned processing, is undertaken. No wastes should be accepted at the facility without sampling and testing being carried out, with the exception of unused, outdated or off-specification products which have not been subsequently contaminated (and for which appropriate MSDS or product data sheets are available).

78. A Waste Analysis Plan (WAP) should be prepared and maintained documenting the procedures that should be used to obtain a representative sample of a waste and to conduct a detailed chemical and physical analysis of this representative sample. A WAP should address measures to identify potentially reactive, and incompatible wastes[4]. The WAP should comprise testing of a representative sample of waste to qualify it for use at the facility (for waste pre-acceptance purposes); testing of incoming waste shipments to verify its constituents (for waste acceptance purposes); and testing of samples taken during or after waste pre-processing or blending to verify the quality of the resultant stream.

79. Operators should ensure that the technical appraisal is carried out by suitably qualified and experienced staff who understand the capabilities of the facility.

80. Records relating to the pre-acceptance should be maintained at the facility for cross-referencing and verification at the waste acceptance stage. The information should be recorded and referenced to the waste stream so that it is available at all times. The information must be regularly reviewed and kept up to date with any changes to the waste stream.

3.2.2 On-site acceptance

81. On-site verification and testing should take place to confirm the characteristics of the waste, and the consistency with the pre-acceptance information. Acceptance procedures should address:

- Measures to deal with pre-approved wastes arriving on-site, such as a pre-booking system to ensure that sufficient capacity is available;
- Vehicle waiting and traffic control;
- Procedures for checking paperwork arriving with the load;
- Procedures for load inspection, sampling and testing;

[4] The U.S. EPA document, "A Method of Determining the Compatibility of Hazardous Wastes" (EPA-600/2-80-076), contains procedures to evaluate qualitatively the compatibility of various categories of wastes.

- Criteria for the rejection of wastes and the reporting of all non-conformances;
- Record keeping; and
- Procedures for periodic review of pre-acceptance information.

82. Wastes should not be accepted without detailed written information identifying the source, composition and hazard of the waste.

83. Where facilities provide a service to emergency services such as the removal of spillages or fly-tipped hazardous wastes, there may be situations where the operator is unable to adhere to established pre-acceptance and/or acceptance procedures. In such instances, the operator should communicate the occurrence to the competent authorities immediately.

Arrival

84. Hazardous wastes should be received under the supervision of a suitably qualified and trained person, and only if sufficient storage capacity exists and the site is adequately manned. All wastes received at the facility should initially be treated as being unknown and hazardous until compliance with specifications has been positively verified.

85. Waste delivery should accompanied by a suitable description of the waste, including name and address of the generator; name and address of the transporter; waste classification/description; volume/weight; and hazard(s) of the waste (such as, flammability, reactivity, toxicity or corrosivity). Documentation accompanying the shipment should be reviewed and approved (including the hazardous waste manifest documentation, if applicable), and any discrepancies should be resolved before the waste is accepted. If discrepancies cannot be resolved, the shipment should be rejected back to the original generator, or at his request, to an alternate facility.

86. Where possible, waste loads should be visually inspected. Containers should be checked to confirm quantities against accompanying paperwork. Containers should be clearly labelled in accordance with applicable regulations for the transport of dangerous goods and should be equipped with well-fitting lids, caps and valves secure and in place. Drums and containers should be inspected for leaks, holes, and rust. Any damaged, corroded or unlabelled drum should be classified as ‘non-conforming’ and dealt with appropriately.

87. All incoming loads should be weighed, unless alternative reliable volumetric systems linked to specific gravity data are available.

Inspection

88. Wastes should not be accepted at the facility without thorough inspection being carried out. Reliance solely on written information supplied should not be acceptable, and physical verification and analytical confirmation should be required, to the extent necessary to verify that it meets permit specifications and regulatory requirements. All wastes, whether for processing or simply storage, should be sampled and undergo verification and testing, according to the frequency and protocol defined in the WAP (except unused, outdated or off-specification products which have not been subsequently contaminated).

89. On-site verification and testing should take place to confirm:

- The identity and description of the waste;
- Consistency with pre-acceptance information; and

– Compliance with the facility permit.

90. Techniques for inspection vary from simple visual assessment to full chemical analysis. The extent of the procedures adopted will depend upon waste chemical and physical composition and variation; known difficulties with certain waste types or of a certain origin; specific sensitivities of the installation concerned (for example, certain substances known to cause operational difficulties); and the existence or absence of a quality controlled specification for the waste, among others. (Karstensen, 2008a)

91. The facility should have a designated sampling or reception area. Containerised waste should be unloaded in this area, only if adequate space is available, and temporarily stored pending further inspection (sampling and sample analysis); wastes should be segregated immediately to remove possible hazards due to incompatibility. Sampling should be performed at the earliest possible time, preferably no later than 24 hours after unloading. During this period, wastes should not be bulked, blended or otherwise mixed. Bulk wastes should be inspected and accepted for processing prior to unloading.

92. Sampling should comply with specific national legislation, where it exists, or with international standards. Sampling should be directly supervised by laboratory staff, and in countries where regulations do not exist, qualified staff should be appointed. Sampling procedures should include well-established procedures such as those developed by the American Society for Testing and Materials (ASTM), the European Committee for Standardization (CEN), and/or the United States Environmental Protection Agency (EPA). A record of the sampling regime for each load and justification for the selected option should be maintained at the installation.

93. Samples should be analysed by a laboratory (preferably accredited) with robust QA/QC methods and suitable record keeping, at the speed required by facility procedures. Particularly for hazardous wastes, this often means that the laboratory needs to be on-site.

94. Typically, waste shipments are sampled and analyzed for a few key chemical and physical parameters (fingerprint analysis) to substantiate the waste composition designated on the accompanying paperwork (manifest and/or other shipping paper). The selection of key parameters must be based on sufficient waste profile knowledge and testing data to ensure accurate waste representation. When selecting fingerprint parameters, consideration should be given to those parameters that can be used to: identify wastes that are not permitted; determine whether the wastes are within the facility's operational acceptance limits; identify the potential reactivity or incompatibility of the wastes; and indicate any changes in waste composition that may have occurred during transportation or storage. Should the results of the fingerprint testing of a given waste stream fall outside the established tolerance limits, the waste may be re-evaluated for possible acceptance to prevent the unnecessary movement of waste back and forth between the generator and the installation when waste can be managed by the facility. Re-evaluation should consider facility conditions for storage and processing; additional parameter analyses performed as deemed appropriate by the operator (and established in the WAP); and permit requirements.

95. The inspection scheme should include (Karstensen, 2008a): assessment of combustion parameters; blending tests on liquid wastes prior to storage; control of flashpoint; and screening of waste input for elemental composition, for example by ICP, XRF and/or other appropriate techniques.

96. Wastes should be moved to the storage area only after its acceptance. Should the inspection or analysis indicate that the wastes fail to meet the acceptance criteria (including damaged or unlabelled drums), then such loads should be stored in a dedicated area allocated for non-conforming waste storage (quarantine area), and dealt with appropriately.

97. All areas where hazardous waste is handled should have an impervious surface with a sealed drainage system. Attention should be given to ensuring that incompatible substances do not come into contact resulting from spills from sampling, for example, within a sump serving the sampling point. Absorbents should be made available.

98. Suitable provisions should be made to verify that wastes being received at the facility are not radioactive. Plastic scintillation detectors are one type of detector used.

99. After being accepted for processing, containerised waste should be labelled with the date of arrival on-site and primary hazard class. Where containers are bulked, the earliest date of arrival of the bulked wastes should be transposed from the original container onto the bulk container. A unique reference number should be applied to each container for the purpose of the in-plant waste tracking system.

3.2.3 Non-conforming waste

100. The operator should have clear and unambiguous criteria for the rejection of wastes (including wastes that fail to meet the acceptance criteria, and damaged, corroded or unlabelled drums), together with a written procedure for tracking and reporting such non-conformance. This should include notification to the customer/waste generator and competent authorities.

101. The operator should also have a clear and unambiguous policy for the subsequent storage (including a maximum storage volume) and disposal of such rejected wastes. This policy should achieve the following:

- Identify the hazards posed by the rejected wastes;
- Label rejected wastes with all information necessary to allow proper storage and segregation arrangements to be put in place; and
- Segregate and store rejected wastes safely pending removal within a reasonable time (where possible, no more than five working days).

102. Wastes that do not fulfil the acceptance criteria of the plant should be sent back to the waste generator, unless an agreement is reached with the generator to ship the rejected waste to an alternative authorised destination.

3.2.4 In-plant tracking system

103. An internal tracking system and stock control procedure should be in place for all wastes, beginning at the pre-acceptance stage, to guarantee the traceability of waste processing and to enable the operator to:

- Prepare the most appropriate waste blend;
- Prevent unwanted or unexpected reactions;
- Ensure that the emissions are either prevented or reduced; and
- Manage the throughput of wastes.

104. The tracking system (which may be a paper system, an electronic system, or a combination of both), should ‘follow’ the waste during its acceptance, storage, processing and removal off-site. It should consequently be possible at any time for the operator to identify where a specific waste is

on the facility, and the length of time it has been there. Records should be held in an area well removed from hazardous activities to ensure their accessibility during any emergency.

105. Once a waste has entered bulk storage or a treatment process, the tracking of individual wastes will not be feasible. However, records should be maintained to ensure sufficient knowledge is available as to what wastes have entered a particular tank, storage pit or other enclosure. For example, it is necessary to keep track of residues that will be building up within a vessel between de-sludging events in order to avoid any incompatibility with incoming wastes.

106. For bulk liquid wastes, stock control would involve maintaining a record of the route through the process, whereas drummed waste control should utilise the individual labelling of each drum to record the location and duration of storage.

107. The in-plant waste tracking system should hold all the information generated during pre-acceptance, acceptance, storage, processing and removal off-site. Records should be made and kept up to date on an ongoing basis to reflect deliveries, on-site treatment and dispatches. The tracking system should operate as a waste inventory/stock control system and include as a minimum:

- A unique reference number;
- Details of the waste generator and intermediate holders;
- Date of arrival on-site;
- Pre-acceptance and acceptance analysis results;
- Container type and size;
- Nature and quantity of wastes held on-site, including identification of associated hazards;
- Details on where the waste is physically located; and
- Identification of staff who have taken any decisions on acceptance or rejection of wastes.

108. The system adopted should be capable of reporting on all of the following:

- Total quantity of waste present on-site at any one time, in appropriate units;
- Breakdown of waste quantities being stored pending on-site processing;
- Breakdown of waste quantities on-site for storage only, that is, awaiting onward transfer;
- Breakdown of waste quantities by hazard classification;
- Indication of where the waste is located relative to a site plan;
- Comparison of the quantity on-site against total permitted; and
- Comparison of time the waste has been on-site against permitted limit.

3.3. Waste Storage and Handling

109. Once it has been determined that the waste is suitable for the installation, the operator should have in place systems and procedures to ensure that wastes are transferred to appropriate storage safely.

110. The issues for the operator to address in relation to measures for waste storage on the installation should include the following:

- Location of storage areas;
- Storage area infrastructure;
- Condition of tanks, drums, vessels and other containers;
- Stock control;
- Segregated storage;
- Site security; and
- Fire risk.

3.3.1 Design considerations

111. Transfer and storage areas should be designed to manage and contain accidental spills. This requires that:

- Adequately bunded and sealed storage areas, which are impermeable and resistant to the stored materials, should be provided to prevent spills from spreading and seeping into the soil;
- All spills should be collected, placed in a suitable container, and stored for disposal in the kiln;
- Incompatible wastes should be prevented from mixing in case of a spill;
- All connections between tanks should be capable of being closed via valves, and overflow pipes should be directed to a contained drainage system (that is, the relevant bunded area or another vessel);
- Leak free equipment and fittings should be installed whenever possible;
- Measures to detect leaks and take appropriate corrective action should be provided;
- Contaminated runoff should be prevented from entering storm drains and water courses (any such runoff should be collected and stored for disposal in the kiln); and
- Adequate alarms for abnormal conditions should be provided.

112. Storage design should be appropriate to maintain the quality of the wastes during the storage time. Segregated storage is necessary to prevent incidents from incompatible wastes and as a means of preventing escalation should an incident occur. Individual storage requirements on a particular installation will be dependent on a full assessment of risk.

113. Storage characteristics should consider the properties of the most hazardous waste that can be accepted at the facility. In general, the storage of wastes needs, additionally, to take into account the unknown nature and composition of wastes, as this gives rise to additional risks and uncertainties. In many cases, this uncertainty means that higher specification storage systems are applied for wastes than for well-characterised raw materials

114. Containerised wastes should be stored under cover, protected from heat and direct sunlight, unless the waste is known to be unaffected by ambient conditions (sunlight, temperature, rain).

115. The design should prevent accumulation of hazardous wastes beyond the allowable period of time in the case of containerised wastes and should consider mixing or agitation to prevent settling of solids in the case of liquid wastes. It may be necessary to homogenise tank contents with mechanical or hydraulic agitators. Depending on the waste characteristics, some tanks may need to be heated and insulated.

116. Tanks, pipelines, valves, and seals must be adapted to the waste characteristics in terms of construction, material selection, and design. They must be sufficiently corrosion proof, and offer the option of cleaning and sampling.

117. Adequate ventilation should be provided in consideration to applicable work exposure guidelines (periodic monitoring for VOC emissions should be considered).

118. A fire protection system that meets all standards and specifications from local authorities (for example, local fire department) should be provided. Automatic fire detection systems should be used in waste storage areas as well as for fabric filters and electrostatic precipitators (ESP), electrical and control rooms, and other identified risk areas. Continuous automatic temperature measurement of the surface of wastes in the storage pits can be used to trigger an acoustic alarm in case of temperature variations.

119. Automatic fire suppression systems should be used in some cases, most commonly when storing flammable liquid waste although also in other risk areas. Foam and carbon dioxide control systems provide advantages in some circumstances, for example, for the storage of flammable liquids. Water systems with monitors, water cannons with the option to use water or foam, and dry powder systems are commonly used.

3.3.2 Operational considerations

120. There should be written procedures and instructions in place for the unloading, handling, and storage of wastes on-site. It should be ensured that chemical incompatibilities guide the segregation required during storage. Compliance with such procedures should be audited regularly.

121. To avoid the need for additional handling and transfer, a common practice is to ensure, as far as possible, that hazardous wastes are stored in the same containers (drums) that were used to deliver the wastes to the facility.

122. Designated routes for vehicles carrying specific hazardous wastes should be clearly identified within the facility. On-site transportation should be performed in a manner which minimizes risk to the health and safety of employees, the public and the environment. The operator should ensure that vehicles are fit for purpose with respect to compliance with relevant regulations. All loads should be properly identified, segregated according to compatibility (so that any potential spills do not create chemical safety hazards), and secured to prevent sliding or shifting during transport. Personnel should be directed and trained to use equipment only as intended, and not to exceed the rated capacity of containers, vehicles, and other equipment.

123. Appropriate signs indicating the nature of hazardous wastes should be in place at storage, stockpiling, and tank locations.

124. Containers should be kept in good condition (free of dents, not leaking or bulging), and closed when not removing waste. Container storage areas should be inspected at least weekly.

125. Maintenance work should be authorized by plant management, and carried out once a supervisor has checked the area and necessary precautions have been taken. Special procedures, instructions, and training should be in place for routine operations such as:

- Working at heights, including proper tie-off practices and use of safety harnesses;
- Confined space entry where air quality, explosive mixtures, dust, or other hazards may be present;
- Electrical lock-out, to prevent accidental reactivation of electrical equipment undergoing maintenance; and
- 'Hot works' (welding, cutting, etc.) in areas that may contain flammable materials.

126. The following measures should be considered to strengthen safety:

- Storage areas should be kept clear of uncontrolled combustible materials;
- Whenever there is a risk that has not been avoided or controlled by engineering controls or other means, standard safety signs and information signs should be provided;
- Where the eyes or body of any person may be exposed hazardous wastes, emergency showers and eye wash stations should be provided within the work area for immediate emergency use (consideration should be given to the possible need for multiple emergency shower installations based upon access distance and the possibility that more than one person may be affected at the same time);
- Adequate alarms should be provided to alert all personnel about emergency situations;
- Communications equipment should be maintained at the site so that the control room and the local fire department can be contacted immediately in case of a fire; and
- Electrical equipment should be grounded and appropriate anti-static devices selected.

3.4. Waste Pre-processing

127. Wastes used in cement kilns should be homogenous with a pre-specified size distribution, and have a stable chemical composition and heat content, so as not to detract from normal kiln operation, product quality, or the site's normal environmental performance. For optimum operation, kilns require very uniform waste material flows in terms of quality and quantity. For certain types of waste this can only be achieved by its pre-processing.

128. Waste pre-processing can include drying, shredding, grinding or mixing depending on the type of waste, and is usually done in a purpose made facility, which may be located outside or inside the cement plant.

129. Liquid waste fuels are normally prepared by blending different wastes with suitable calorific values and chemistry (like spent solvents or used oil). Normally, only simple pre-treatment is necessary (removal of bottoms, sediments and water). In some cases, for example machining oil/emulsion, chemical processes are necessary to remove metallic pollutants and additives. The extent of solid waste processing, such as sorting, crushing, or pelletizing, depends on the specific application.

3.4.1 Design considerations

130. Facility layout should be carefully considered to ensure access for day-to-day operations, emergency escape routes, and maintainability of the plant and equipment.

131. Recognized standards should be applied to the design of installations and equipment. Any modifications should be documented.

132. Operations should be assessed for health and safety risks or concerns to ensure that equipment is safe and to minimize risks of endangering people or installations, or damaging the environment. Appropriate procedures should be used to assess risks or hazards for each stage of the design process. Only competent and qualified personnel should undertake or oversee such hazard and operability studies.

3.4.2 Operational considerations

133. Mixing and homogenisation of wastes will generally improve feeding and combustion behaviour. Mixing of wastes can involve risks and should be carried out according to a prescribed recipe.

134. Techniques used for waste pre-processing and mixing are wide ranging, and may include:

- Mixing and homogenising of liquid wastes to meet input requirements, for example, viscosity, composition and/or heat content;
- Shredding, crushing, and shearing of packaged wastes and bulky combustible wastes, for example, tyres; and
- Mixing of wastes in a storage pit or similar enclosure using a grab or other machine.

135. Crane operators should be able to identify potentially problematic loads (for example, baled wastes, discrete items that cannot be mixed or will cause loading/feeding problems) and ensure that these are removed, shredded or directly blended (as appropriate) with other wastes.

136. General tidiness and cleanliness contribute to an enhanced working environment and can allow potential operational problems to be identified in advance. The main elements of good housekeeping are:

- The use of systems to identify and locate/store wastes received according to their risks;
- The prevention of dust emissions from operating equipment;
- Effective wastewater management; and
- Effective preventive maintenance.

3.5. Pre-processing Plant Closure/Decommissioning

137. Closure is the period directly after the facility stops its normal operations. During this period the facility stops accepting hazardous waste; completes storage and processing of any wastes left on site; and disposes or decontaminates equipment, structures, and soils, restoring the site, insofar as possible, to its original condition or in keeping with the intended land use. Planning for decommissioning of the facility should be undertaken during the initial stages of the overall project. By integrating decommissioning requirements into the facility design at the outset, the site

development plan should be compatible with the proper closure requirements when the operation of the facility has ended.

138. Operators should be required to close the facility in a manner that minimizes the further need for maintenance, and prevents the escape of any hazardous contaminants to the environment. To ensure that the facility is properly closed, a closure plan should be prepared identifying the steps necessary to partially or completely close de facility, including:

- Procedures for handling removed inventory;
- Procedures for decontamination and/or disposal;
- Procedures to confirm effectiveness of decontamination, demolition and/or excavation (including procedures for performing sample collection and analysis);
- Health and safety plan addressing all health and safety concerns pertinent to closure activities; and
- Security system to prevent unauthorized access to the areas affected by closure activities.

139. To prevent a facility from ceasing operations and failing to provide for the potentially costly closure requirements, operators should be required to demonstrate that they have the financial resources to properly conduct closure in a manner that protects human health and the environment.

140. To minimise decommissioning problems and associated environmental impacts, the European IPPC Bureau (2006) recommends for existing installations where potential problems are identified, putting in place a programme of design improvements. These designs improvements would need to ensure that underground tanks and piping are avoided (if not possible to replace, then operators should provide secondary containment or develop a suitable monitoring programme), and that there is provision for the draining and clean-out of vessels and piping prior to dismantlement, among others.

3.6. Environmental Aspects

3.6.1 VOC, odours, and dust

141. Emissions to air from waste pre-processing will depend on the types of wastes treated and the processes used. Emission monitoring and reporting must be performed according to locally applicable regulations.

142. Abatement techniques should be in place as needed. Dust is usually reduced by bag filters. Countermeasures for noise and odours should be considered. Common reduction techniques for VOC, pending monitoring results, may include biological treatment, activated carbon and thermal treatment, among others.

3.6.2 Drums and ferrous metals

143. Empty drums and ferrous metals removed by magnetic separators should disposed of in accordance with the requirements of local authorities. Metal scrap not containing any contaminants to an extent to render it hazardous can be recycled for steelmaking. Empty drums that formerly contained wastes and are in good condition can be sent to authorised drum washers/recyclers.

3.6.3 Wastewater

144. Discharges of wastewater to surface water should not result in contaminant concentrations in excess of local ambient water quality criteria or, in the absence of local criteria, other sources of ambient water quality. Receiving water use and assimilative capacity, taking other sources of discharges to the receiving water into consideration, should also influence the acceptable pollution loadings and effluent discharge quality.

145. Discharges into public or private wastewater treatment systems should meet the pre-treatment and monitoring requirements of the sewer treatment system into which it discharges, and should not interfere, directly or indirectly, with the operation and maintenance of the collection and treatment systems, or pose a risk to worker health and safety, or adversely impact characteristics of residuals from wastewater treatment operations.

3.7. Emissions Monitoring and Reporting

146. Emissions and air quality monitoring programs provide information that can be used to assess the effectiveness of emissions management strategies. A systematic planning process is recommended to ensure that the data collected are adequate for their intended purposes (and to avoid collecting unnecessary data). An air quality monitoring program should consider baseline air quality monitoring at and in the vicinity of the facility to assess background levels of key pollutants.

147. When wastewater is discharged, a wastewater and water quality monitoring program with adequate resources and management oversight should be developed and implemented to meet the objective(s) of the monitoring program.

148. The parameters selected for monitoring should be indicative of the pollutants of concern from the process, and should include parameters that are regulated under compliance requirements. Monitoring programs should apply national or international methods for sample collection and analysis, such as those published by the International Organization for Standardization (ISO), CEN or the United States EPA. Sampling should be conducted by, or under, the supervision of trained individuals. Analysis should be conducted by entities permitted or certified for this purpose. Sampling and analysis QA/QC plans should be applied and documented to ensure that data quality is adequate for the intended data use. Monitoring reports should include QA/QC documentation.

4.Co-processing in Cement Kilns

4.1. Introduction

149. For optimal use in cement kilns (co-processing with 'zero additional emissions') alternative fuels and raw materials need to be fed to the kiln via appropriate feed points and in adequate proportions, with proper waste quality and emission control systems implemented.

150. Co-processing has the following characteristics during the production process (GTZ/Holcim, 2006):

- The alkaline conditions and the intensive mixing favour the absorption of volatile components from the gas phase. This internal gas cleaning results in low emissions of components such as SO_2, HCl, and most of the heavy metals, with the exception of mercury, cadmium and thallium.
- The clinker reactions at 1450°C allow the chemical binding of metals and the incorporation of ashes to the clinker.
- The direct substitution of primary fuel by high calorific waste material causes a higher efficiency on energy recovery in comparison to other 'waste to energy' technologies (destruction of organics).

4.2. Operational Requirements

151. Safe and responsible co-processing requires careful selection of the feed points in the kiln system as well as comprehensive operational control according to the specific characteristics and volumes of the waste material.

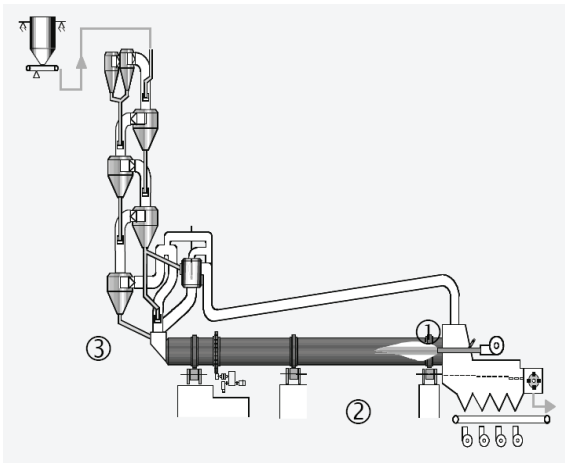
4.2.1 Feed point selection

152. Many cement kilns co-process waste commercially (that is, they accept waste from off-site generators), in most cases for use as a fuel substitute in the production of cement clinker. Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. For long kilns, this means that the solid waste is introduced mid-kiln, and for preheater/precalciner kilns that it is introduced onto the feed shelf in the high-temperature section.

153. In the case of hazardous wastes, complete destruction of combustible toxic compounds such as halogenated organic substances has to be ensured through proper temperature and residence time. In general, waste should be fed through either the main burner or the secondary burner for preheater/precalciner kilns. In the main burner conditions will always be favourable. For the secondary burner it should be ensured that the combustion zone temperature is maintained over 850°C for a sufficient residence time (two seconds).

Figure 3: Temperatures and residence times during cement production

Characteristics	Temperature and time
Temperature at main burner ① of the rotary kiln ②	>1450°C (material) >1800°C (flame temperature)
Residence time at main burner	>12-15 seconds > 1200°C >5-6 seconds > 1800°C
Temperature at precalciner ③	> 850°C (material) >1000°C (flame temperature)
Residence time at precalciner	> 2-6 seconds > 800°C



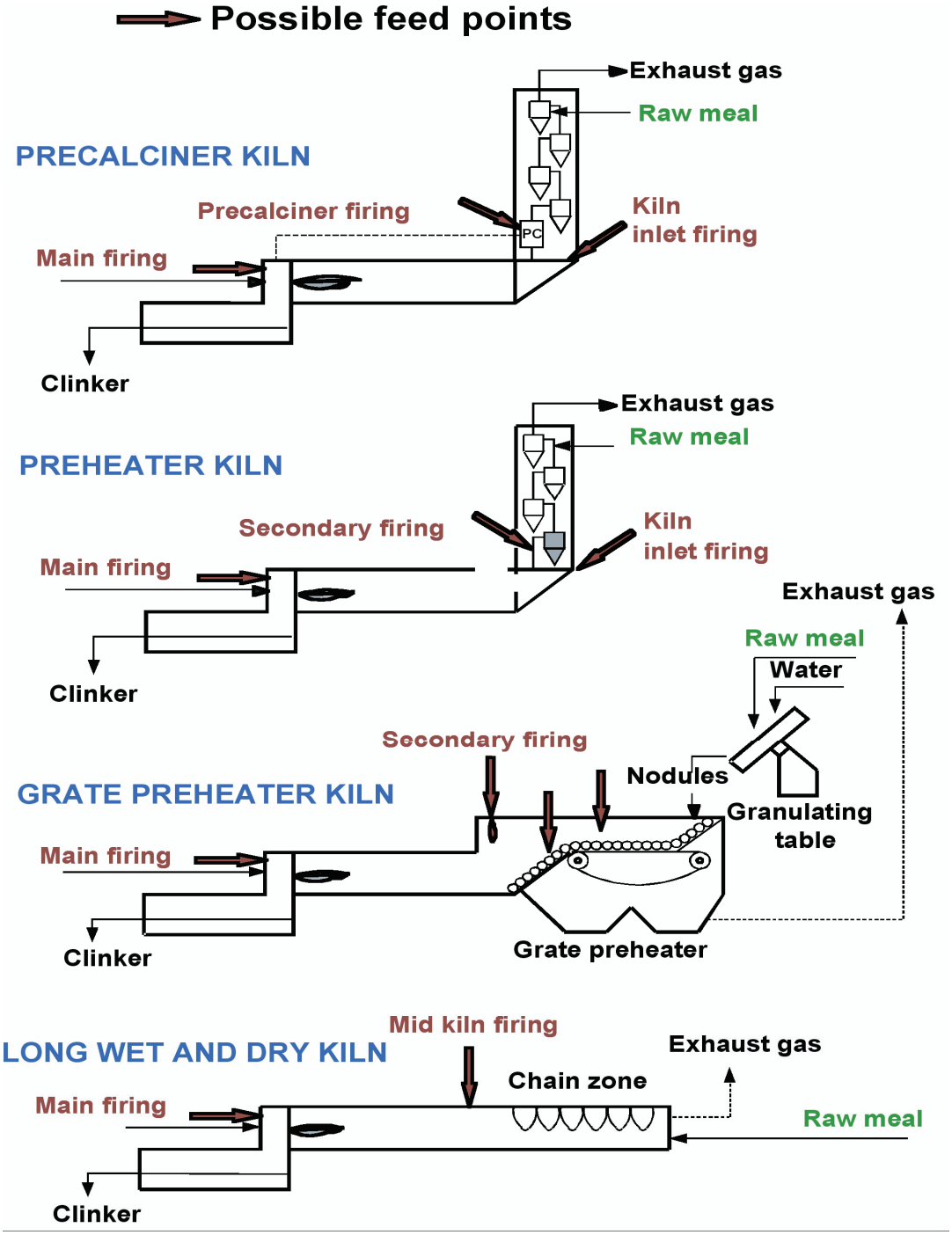
154. If hazardous waste with a content of more than 1 percent of halogenated organic substances (expressed as chlorine) is fed to the kiln, the temperature should be maintained at 1100°C for at least two seconds.

155. Alternative raw materials are typically fed to the kiln system in the same way as traditional raw materials, for example, via the normal raw meal supply. Alternative raw materials containing components that can be volatilised at low temperatures (for example, solvents) should be fed into the high temperature zones of the kiln system. Alternative raw materials containing volatile (organic and inorganic) components should not be fed to the kiln via the normal raw meal supply unless it has been demonstrated by controlled test runs in the kiln or by adequate laboratory tests that undesired stack emissions can be avoided.

156. Adequate feed points should be selected according to the physical, chemical, and (if relevant) toxicological characteristics of the waste material used (see Figure 4). Different feed points can be used to introduce waste materials into the cement production process. The most common ones being:

- Via the main burner at the rotary kiln outlet end;
- Via a feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
- Via secondary burners to the riser duct;
- Via precalciner burners to the precalciner;
- Via a feed chute to the precalciner (for lump fuel); and
- Via a mid kiln valve in the case of long wet and dry kilns (for lump fuel).

Figure 4. Possible waste feed points



4.2.2 Kiln operation control

157. The impact of waste materials on the total input of circulating volatile elements such as chlorine, sulphur, or alkalis should be assessed very carefully prior to acceptance, as they may cause operational troubles in a kiln. Specific acceptance criteria for these components should be set by each facility based on the process type and on the specific kiln conditions.

158. The general principles of good operational control of the kiln system using conventional fuels and raw materials should be applied. In particular, all relevant process parameters should be measured, recorded, and evaluated continuously. Kiln operators should be trained accordingly, with special focus on requirements related to the use of waste materials - including health, safety, and environmental emission aspects.

159. Waste should never be fed during start-up and shutdown. For upset conditions of the kiln, written work instructions describing the strategy to disconnect the waste feed to ensure minimum operational stability conditions should be available and known to the kiln operators.

160. The mineral content of the waste may change the characteristics of the clinker. The raw mix composition should be adjusted accordingly to stick to the given chemical set points. Input limits for chlorine, sulphur, and alkalis should be defined, and operational set points should be strictly observed. Bypass installations to increase waste use should only be considered if appropriate solutions for the management of the bypass dust generated have been identified.

4.3. Environmental Aspects

4.3.1 Air emissions

161. The main emissions from cement kiln systems are emissions to air, whether alternative fuels and/or raw materials are being used or not. These emissions may include, inter alia, dust (particulate matter), NOx, CO, CO_2, SO_2 and other oxides of sulphur, metals and their compounds, HCl, HF, ammonia (NH_3), PCDDs, PCDFs, benzene, toluene, xylene, polycyclic aromatic hydrocarbons (PAH), chlorobenzenes and PCBs (SBC, 2007; European IPPC Bureau, 2009). The sources of these emissions are outlined in Annex 4.

162. Existing and potential control technologies are described by Greer (2003) and Karstensen (2008b), while details on best available techniques (BAT) are provided by the European IPPC Bureau (2009). The prevention or minimization of the formation and subsequent release of unintentional POPs from cement kilns co-processing hazardous waste is the subject of Article 5 of the Stockholm Convention. Guidance on applicable best available techniques and best environmental practices (BEP) is provided in the "Guidelines on Best Available Techniques and Provisional Guidance on Best Environmental Practices Relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants", which were finalized by the Stockholm Convention Expert Group on Best Available Techniques and Best Environmental Practices in December 2006.

163. For reference purposes, emission limits for cement kilns co-processing hazardous wastes are provided in Annex 5. Competent authorities should consider establishing a maximum permissible period of any technically unavoidable stoppages, disturbances, or failures of the purification devices or the measurement devices, during which the emissions into the air may exceed the prescribed emission limit values.

4.3.2 Cement kiln and bypass dust

164. All cement plants generate a fine dust from the kiln line, collectively labelled CKD. CKD composition varies among plants and even over time from a single kiln line, but includes particulates representing the raw mix at various stages of burning, particles of clinker, and even particles eroded from the refractory brick and/or monolithic linings of the kiln tube and associated apparatus (Van Oss, 2005). Dust is also discarded from alkali bypass systems (installed to avoid

excessive build-up of alkali, chloride and/or sulphur), however bypass dust consists of fully calcined kiln feed material.

165. The majority of CKD and bypass dust is recycled directly back to the cement kiln and/or cement clinker grinder, thus avoiding disposal. However, some dust may need to be periodically removed from the system due to increasing concentrations of various contaminants that may compromise the quality of the clinker. Dust that cannot be recycled back into the process is removed from the system and often collected onsite in piles or monofills. CKD is frequently used for beneficial agricultural applications.

166. To ensure the protection of public health and the environment, discarded bypass dust or CKD from facilities using hazardous wastes as supplementary fuels or raw materials, should be analyzed for leachate (metals and organics) if they are to be land disposed, to prevent groundwater contamination. The analysis should be conducted during the trial burn in addition to ongoing testing that may be required by local regulatory authorities. Releases of dust to air should also be controlled.

4.3.3 End-product control

167. Final products such as clinker or cement are subject to regular control procedures required by the usual quality specifications as laid down in applicable national or international quality standards.

168. Co-processing should not alter the quality of the cement being produced: the product (clinker, cement, concrete) should not be abused as a sink for heavy metals; the product should not have any negative impact on the environment as, for example, demonstrated with leaching tests on concrete and/or mortar; and the quality of cement shall allow end-of-life recovery.

169. The heavy metal content of clinker made without the use of waste varies significantly depending on the geographical and/or geological location of the raw materials. Lengthy investigations have shown that the effect of waste on the heavy metals content of clinker is marginal on a statistical basis. The one exception is that the bulk use of tires will raise zinc levels.

170. Organic pollutants in the materials fed to the high temperature zone of the kiln system are completely destroyed, and the inorganic components are incorporated into the end product.

171. The main results of the many leaching studies done to asses the environmental impacts of heavy metals embedded in concrete are as follows (GTZ/Holcim, 2006):

- The leached amounts of all trace elements from monolithic concrete (service life and recycling) are below or close the detection limits of the most sensitive analytical methods;
- No significant differences in leaching behaviour of trace elements have been observed between different types of cements produced with or without alternative fuels and raw materials;
- The leaching behaviour of concrete made with different cement types is similar;
- Leached concentrations of some elements such as chromium, aluminium and barium may, under certain test conditions, come close to limits given in drinking water standards; hexavalent chromium in cement is water-soluble and may be leached from concrete at a level higher than other metals, so chromium inputs to cement and concrete should be as limited as possible;

- Laboratory tests and field studies have demonstrated that applicable limit values (for example, groundwater or drinking water specifications) are not exceeded as long as the concrete structure remains intact (for example, in primary or service life applications);
- Certain metals such as arsenic, chromium, vanadium, antimony, or molybdenum (so-called 'oxyanions') may have a more mobile leaching behaviour, especially when the mortar or concrete structure is destroyed through crushing or other size-reduction processes (e.g. in recycling stages such as use as aggregates in road foundations, or in end-of-life scenarios such as landfilling); and

172. As there are no simple and consistent relations between the leached amounts of trace elements and their total concentrations in concrete or in cement, the trace element content of cements cannot be used as environmental criteria.

173. Assessments of the environmental quality of cement and concrete are typically based on the leaching characteristics of heavy metals to water and soil. Various exposure scenarios should be considered (GTZ/Holcim, 2006):

- Exposure of concrete structures in direct contact with groundwater ('primary' applications);
- Exposure of mortar or concrete to drinking water in distribution (concrete pipes) or storage systems (concrete tanks) ('service life' applications);
- Reuse of demolished and recycled concrete debris in new aggregates, road constructions, dam fillings etc. ('secondary' or 'recycling' applications); and
- Dumping of demolished concrete debris in landfills ('end-of-life' applications).

174. In cases where the concentration of heavy metals exceeds the normal range found in cements made without alternative fuels and/or materials, leaching tests on mortar and/or concrete should be conducted.

175. For different, real-life concrete and mortar exposure scenarios, different leaching tests and assessment procedures must be applied. Existing standardized test procedures have been developed mainly for waste regulations and drinking water standards. There remains a need for harmonized and standardized compliance test procedures based on the exposure scenarios as outlined above.

4.4. Monitoring

176. Emission monitoring is necessary to allow authorities to check compliance with the conditions in operating permits and regulations. For this purpose use of the following is good practice (European IPPC Bureau, 2003):

- Standard methods of measurement;
- Certified instruments;
- Certification of personnel; and
- Accredited laboratories.

4.4.1 Process monitoring

177. To control kiln processes, continuous measurements are recommended for the following parameters (European IPPC Bureau, 2009):

- Pressure
- Temperature
- O_2
- CO
- NOx
- SO_2

4.4.2 Emissions monitoring

178. To accurately quantify the emissions, continuous measurements are recommended for the following parameters:

- Exhaust gas flow rate
- Moisture
- Temperature
- O_2
- Dust (particulate matter)
- NOx
- SO_2
- CO
- Total organic compounds (TOC)

179. The operator should assure proper calibration, maintenance, and operation of the continuous emission monitoring systems (CEMS). A quality assurance program should be established to evaluate and monitor CEMS performance on a continual basis.

180. Occasional monitoring (minimum once per year) is appropriate for the following substances:

- Metals (Hg, Cd, Tl, As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V) and their compounds
- HCl
- HF
- NH_3
- PCDDs/PCDFs

181. It is also possible to measure and monitor NH_3, Hg, HCl and HF continuously, and to sample PCCDs/PCDFs and PCBs continuously for analysis from 1 to 30 days (European IPPC Bureau, 2009).

182. Performance tests should be conducted to demonstrate compliance with the emission limits and performance specifications for continuous monitoring systems, when the kiln operates under normal operating conditions.

183. Measurements of the following may be required under special operating conditions (European IPPC Bureau, 2009):

- Benzene, toluene and xylene (BTX)
- Polycyclic aromatic hydrocarbons (PAHs), and
- Other organic pollutants (for example, chlorobenzenes, PCBs including coplanar congeners, chloronaphthalenes, etc.)

184. Depending on the waste materials co-processed, the process conditions and the relevance of the emissions, it may be necessary to carry out additional measurements. The requirements of national regulations have to be considered as well. In case of disposal of wastes consisting of, containing or contaminated with persistent organic pollutants, the DRE should be determined (UNEP, 2007).

4.4.3 Environmental monitoring

185. Where there are justifiable concerns, an ambient air-monitoring programme may be required to monitor the environmental impact from the plant. This should assess environmental levels of key pollutants identified as a priority for control. The arrangements should include control and downwind locations, including the area of maximum ground level deposition from stack emissions. A meteorological station should be provided for the duration of the ambient sampling exercise in a location free of significant interference from buildings or other structures.

4.4.4 Reporting requirements

186. Reporting of monitoring results involves summarising and presenting results, related information and compliance findings in an effective way.

187. Presentation of results for reporting purposes should indicate if exceedances or changes are significant when compared with the uncertainties in measurements and process parameters (European IPPC Bureau, 2003).

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Annex 1. Clinker Production Process

1. Cement production involves the heating, calcining and sintering of a carefully proportioned mixture of calcareous and argillaceous materials, usually limestone and clay, to produce cement clinker, which is then cooled and ground with additives such as gypsum (a setting retardant) to make cement. This process typically requires approximately 2,9 to 6,7 GJ of energy depending on the kiln technology employed (IEA, 2007) and 1,5 to 1,7 tonnes of raw materials per tonne of clinker produced (Szabó et al, 2003); the portion of raw material that does not become clinker is either lost on ignition or becomes CKD (U.S. EPA, 1993). 'Wet' processes also use water to make the raw slurry that feeds the kilns; about 600 kg of water is used in the manufacture of one tonne of cement, some of which is returned to the environment (EA, 2005).

2. Manufacturers use clinker and specific additives in various proportions to produce cements that meet different physical and chemical requirements for specific applications. By far the most common hydraulic cements in use today are either Portland cements or 'blended' cements (van Oss and Padovani, 2003). The great majority of Portland cements made throughout the world are designed for general construction use. The standard specifications with which such cements must comply are similar (albeit not identical) in all countries and various names are used to define the material, such as cement type CEM I in current European standards, Types I and II Portland cement in ASTM specifications used in the U.S., or Ordinary Portland Cement (OPC) in some places. Blended cements, also called composite cements, are mixtures of Portland cement with one or more pozzolanic additives or extenders (sometimes collectively termed 'supplementary cementitious materials'), such as pozzolana (volcanic ashes), certain types of fly ash (from coal-fired powerplants), granulated blast furnace slag, silica fume, or limestone. These materials commonly make up about 5% to 30% by weight of the total blend, but can be higher (van Oss, 2005). The designations for blended cements differ worldwide.

3. Although a variety of cement types are produced worldwide, cement production follows essentially the same process, as described below.

Conventional Raw Materials and Fuel

4. The raw materials for cement must yield the oxides required for clinker in the approximate proportions noted in Table 1, with the major requirement being calcium oxide (CaO). In practical terms this means that naturally occurring calcareous deposits, such as limestone, marl or chalk, which consist essentially of calcium carbonate ($CaCO_3$), are required. Clay or shale typically provides the remaining components. To correct for minor deficiencies in one or more oxides in the primary raw materials, 'corrective' constituents[5] such as iron ore, bauxite or sand, may be added to adapt the chemical composition of the raw mix to the requirements of the process and product specifications (Taylor, 1997; Karstensen, 2007b). Generally, most, but not all, of the raw materials are mined adjacent to or within a few miles of the cement plant.

[5] Sometimes called accessory or 'sweetener' materials (van Oss, 2005).

Table 1. Chemical composition of ordinary Portland cement clinker and conventional raw materials

Constituent	Clinker	Limestone, lime marl, chalk	Clay	Sand	Iron ore	Bauxite
SiO_2	19,71-24,25%	0,5-50%	33-78%	80-99%	4-11%	2,9%
Al_2O_3	3,76-6,78%	0,1-20%	7-30%	0,5-7%		
TiO_2	0,21-0,52%	0,0-0,7%	0,2-1,8%	0,0-0,5%		
$Al_2O_3 + TiO_2$			7-30%	0,5-2%	0,2-3%	57,5%
Fe_2O_3	1,29-4,64%	0,2-5,9%	4,0-15%	0,0-4%		
Mn_2O_3	0,03-0,68%	0,02-0,15%	0,09%	0,051%		
$Fe_2O_3 + Mn_2O_3$		0,1-10%	2-15%	0,5-2%	19-95%	22,8%
CaO	63,76-70,14%	20-55%	0,2-25%	0,1-3%	0,1-34%	2,4%
MgO	0,00-4,51%	0,2-6%	0,3-5%	0,3-0,5%	≤1,5%	0,04%
K_2O	0,31-1,76%	0-3,5%	0,4-5%	0,2-3%	Traces	0,04%
Na_2O	0,03-0,335	0,0-1,5%	0,1-1,5%	0,0-1%	Traces	0,02%
Cl		0,0-0,6%	0,0-1%	Traces		
P_2O_5	0,02-0,27%	0,0-0,8%	0,0-1,0%	0,0-0,1%		
Loss on ignition ($CO_2 + H_2O$)	0,09-1,56%	2-44%	1-20%	≤5	0,1-30%	13,5%

Sources: European Commission (2009) and Cembureau (1999)

5. Natural forms of $CaCO_3$ consist of coarser or finer crystals of calcite. Limestone is microcrystalline $CaCO_3$ with clay as the main impurity. Chalk is a very fine grained, porous marine limestone composed almost entirely of microscopic fossils. The main constituents of shale and clay are clay minerals, finely divided quartz and, sometimes, iron oxides. Traditionally, wet materials (chalk and clay) have been used in 'wet' or 'semi-wet' kiln processes, and dry materials (limestone) have been used in the 'dry' or 'semi-dry' processes (EA, 2005).

6. Around 80-90% of raw material for the kiln feed is limestone; clayey raw material accounts for between 10-15%, although the precise amounts will vary (BGS, 2005). In addition to the chemical composition of the desired product, the proportion of each type of raw material used in a given cement kiln will depend on the composition of the specific materials available to the operator, which is tested on a regular basis.

7. The proportioning process takes into account the ratios of calcium, silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) needed to produce good quality clinker, as well as the 'burnability' of the raw mix (i.e., the requirements in terms of time, temperature, and fuel to process the material) (U.S. EPA, 1993). In addition, kiln operators pay close attention to the presence of 'impurities' in the mixture, including magnesia, sulphur, chlorides, and oxides of potassium and sodium (referred to as 'alkalies'). Magnesia (MgO) can be desirable to some extent because it acts as a flux at sintering temperatures, facilitating the burning process, however MgO levels are carefully monitored because they can lead to the production of clinker that is unsound if not cooled rapidly[6]. Alkalies can react in the cool end of the kiln with sulphur dioxide, chlorides, and carbon dioxide contained in the kiln gas and can lead to operational problems (U.S. EPA, 1993).

[6] Such clinker used to make concrete can cause destructive expansion of hardened concrete through slow reaction with water.

8. The raw materials used in the cement production process naturally contain metals and halogens. Thus, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium, vanadium, zinc, bromine, chlorine, fluorine, and iodine are typically present in the raw materials. The amounts of these components depend on the geological formations from which the raw materials are mined. In addition to the metals and halogens present, the raw materials can contain organic compounds (Mantus, 1992). Average values and range of concentrations of these constituents are presented in Table 2Table 2.

9. Cement production also has high energy requirements, which typically account for 30-40% of the production costs (excluding capital costs). Most cement kilns today use coal and petroleum coke as primary fuels, and to a lesser extent natural gas and fuel oil. As well as providing energy, some of these fuels, especially coal or lignite, which produce significant quantities of ash similar in composition to the argillaceous component.

10. Many plants routinely burn more than one fuel. For example, when firing up a cold kiln, natural gas or fuel oil is commonly used for the slow, warm-up phase necessary to prevent thermal overstressing of the kiln's refractory brick lining. Once the kiln is sufficiently hot, it will be switched over to coal and/or coke (generally petroleum coke) for production operations. (van Oss, 2005)

11. Coal can contain significant quantities of sulphur, trace metals, and halogens, and their concentrations are dependent on the area in which the coal was mined (see Table 3). Sulphur (in the form of SO_3) will vaporize in the kiln to form sulphur dioxide (SO_2), and condense in the form of sulphates. Within the kiln, these sulphates combine with calcium and potassium, causing operational problems in the cool end of the kiln. Halogens are of concern because chlorides can cause operational problems similar to those caused by sulphur. Chlorine concentrations in coal can range from 100 to 2800 parts per million. (U.S. EPA, 1993)

12. Both heat and electricity consumption vary significantly with kiln technology (see Table 4) and, for a given technology, tend to be higher for plants operating multiple kilns than for plants with a single kiln of the same overall capacity. Wet kilns consume more fuel on a unit basis than do dry kilns because of the need to evaporate the water in the slurry feed and the much larger size of the wet kilns.

Table 2. Trace element concentrations (in parts per million) in conventional raw materials (Min = minimum value; Max = maximum value; AV = average value; n.a. = no data available)

Constituent	Limestone Min-Max	(AV)	Marl Min-Max	(AV)	Clay Min-Max	(AV)	Sand Min-Max	(AV)	Iron ore Min-Max	(AV)	Gypsum/anhydrite Min-Max	(AV)
As	0,1-15	(3)	0,2-12	(6)	2-100	(14)	0,4-42	(11)	2-1200	(37)	0,2-3,5	(1,5)
Be	0,01-12	(0,3)	-1	(0,5)	1-7	(3)	0,6-1,5	(1,0)	0,8-2	(1)	0,02-0,9	(0,2)
Cd	0,02-2	(0,2)	0,02-0,5	(0,3)	0,01-1	(0,2)	0,01-1	(0,2)	0,02-15	(6)	0,03-2,3	(0,15)
Co	0,1-7	(3)	n.a.-28	(5)	6-25	(20)	0,3-37	(11)	109-183	(144)	0,02-3,9	(1)
Cr	0,5-184	(14)	1,2-71	(28)	15-260	(85)	1-220	(19)	8-1400	(495)	1-27,3	(8,8)
Cu	5-57	(11)	4,9-35	(12)	10-285	(43)	1,2-85	(10)		(1520)	0,3-12,8	(7)
Hg	0,005-0,1	(0,04)	0,005-0,1	(0,03)	0,01-0,5	(0,2)	0,01-1	(0,02)	n.a.-1	(0,5)	0,00625-1,3	(0,1)
Mn	250-3300	(500)	n.a.-3300	(360)	n.a.-2500	(600)	46-2040	(194)	900-1200	(1090)	n.a.	
Ni	1,4-131	(18)	1,5-57	(16)	7-236	(63)	1-73	(13)	5-815	(331)	0,3-14,5	(5,5)
Pb	0,27-151	(18)	0,3-57	(12)	1-219	(25)	0,7-70	(10)	4-8700	(350)	0,2-20,5	(7)
Sb	0,2-27	(1)	n.a.-27	(4)	0,5-13	(2)	0,3-12	(7)		(26)	0,1-5	(1)
Se	0,4-30	(0,6)		(1)	n.a.-2,5	(0,5)		(1)		(8)	0,6-17	(0,8)
Sn	0,9-24	(4)	n.a.-24	(3)	1,6-30	(5)	1,8-40	(3)	n.a.-500	(25)	n.a.	
Te		(0,7)		(1)		(0,5)		(0,5)	n.a.-13	(10)	n.a.	
Tl	0,05-3	(0,3)	0,05-0,68	(0,6)	0,1-1,6	(0,5)	0,05-1	(0,2)	0,1-400	(2)	0,1-1,0	(0,3)
V	5-80	(26)	n.a.-49	(20)	30-300	(130)	2-240	(50)	10-690	(256)	1-27,8	(13,5)
Zn	0,1-229	(30)	22-79	(48)	2-304	(78)	4,2-112	(25)	24-9400	(3288)	1-59	(19)
Br a/		(5,9)	n.a.		1-58		n.a.		n.a.		n.a.	
Cl a/	50-240		n.a.		15-450		n.a.		n.a.		n.a.	
F a/	100-940		n.a.		300-990		n.a.		n.a.		n.a.	
I a/	0,25-0,75		n.a.		0,2-2,2		n.a.		n.a.		n.a.	

a/ Mantus (1992)

Source: Achternbosch et al. (2003), unless otherwise noted.

Table 3. Trace element concentrations (in parts per million) in primary fuels (Min = minimum value; Max = maximum value; AV = average value; n.a. = no data available)

Constituent	Anthracite Min-Max	(AV)	Bituminous coal Min-Max	(AV)	Lignite Min-Max	(AV)	Petroleum coke Min-Max	(AV)
As	1-200	(9)	n.a.		0,1-12	(0,8)	0,2-0,8	(0,5)
Be	0-8	(1,4)	n.a.		0,04-0,6	(0,2)	0,02-0,03	(0,03)
Cd	0,01-10	(1,0)	n.a.		0,06-2,4	(0,2)	0,04-4	(1)
Co	0,5-43	(9)	n.a.		0,5-4,2	(1)		(2,5)
Cr	1-260	(14)	n.a.		0,9-20	(3,6)	0,9-104	(4,3)
Cu	0,30-60	(18)	n.a.		0,4-15	(1,8)		(2,4)
Hg	0,01-3	(0,3)	n.a.		0,01-0,7	(0,2)	0,01-0,09	(0,05)
Mn	5-356	(58)	n.a.		50-160	(77)	n.a.	
Ni	1-110	(23)	n.a.		0,6-29	(3)	24-355	(263)
Pb	5-270	(27)	n.a.		0,7-34	(3)	1-102	(13)
Sb	0,05-5	(1)	n.a.		0,04-2,5	(0,8)		(0,6)
Se	0-6	(2)	n.a.		0,4-25	(2,6)	n.a.	
Sn	1,3-7,8	(4)	n.a.		0,5-15	(4)		(0,3)
Te	0,2-5,0	(2)	n.a.		0,1-10	(3)	n.a.	
Tl	0,1-5	(1)	n.a.		0,05-0,4	(0,1)	0,04-3,1	(0,5)
V	10-250	(39)	n.a.		0,1-84	(10)	45-1435	(758)
Zn	4,5-405	(63)	n.a.		1-70	(10)	16-220	(16)
Br a/	n.a.		7-11		n.a.		n.a.	
Cl a/	n.a.		100-2800		n.a.		n.a.	
F a/	n.a.		50-370		n.a.		n.a.	
I a/	n.a.		0,8-11,2		n.a.		n.a.	

a/ Mantus (1992)

Source: Achternbosch et al. (2003), unless otherwise noted.

Table 4. Energy requirements for clinker manufacture

Process	Fuel consumption, GJ/tonne
Vertical shaft kiln	3,7-6,6
Wet process	5,9-6,7
Long dry process	4,6
1 stage cyclone preheater	4,2
2 stage cyclone preheater	3,8
4 stage cyclone preheater	3,3
4 stage preheater + precalciner	3,1
5 stage preheater + precalciner	3,0-3,1
6 stage preheater + precalciner	2,9

Source: IEA (2007) and Szabó (2003)

Manufacturing Process

13. Portland cement manufacture begins with the manufacture of clinker followed by the fine grinding of the clinker with gypsum and other additives to make the finished cement product.

Grinding can occur on site or at offsite grinding plants (cement mills). Clinker manufacture itself involves first the quarrying, crushing, and proportioning of raw materials to produce either a raw meal for the dry (and semi-dry) process or a slurry for the wet (and semi-wet) process. Once the material is prepared, it is fed into a kiln where the heating of the raw mix as it moves through the kiln drives a number of chemical and physical processes which are necessary to form the clinker.

14. In the kiln, the raw meal (or slurry in the wet process) is subjected to a thermal treatment process consisting of the consecutive steps of 'drying/preheating', 'calcining', and 'sintering' (also known as 'burning' or 'clinkering'); the various reactions zones are depicted in Figure 1. In the first drying and preheating zone, occurring in a temperature range of <100 to 750°C, residual (free) water is evaporated from the raw meal feed, and clay materials begin to decompose and are dehydrated (removing bound water). Next, in the calcining zone (with materials temperatures ranging from 750 to 1000°C) the material is 'calcined'; that is calcium carbonate ($CaCO_3$) in the limestone is dissociated producing calcium oxide (CaO, lime) and liberating gaseous carbon dioxide (CO_2). Finally, in the burning zone, calcium oxide reacts with silicates, iron, and aluminium to form dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite (denoted in shorthand: C_2S, C_3S, C_3A, and C_4AF respectively). In addition, clinker nodules, typically 3 to 20 mm in diameter, are formed in a semi-solid state in the burning zone, and solidify completely on cooling, which begins in a short cooling zone within the kiln, and continues in a cooler, outside of the cement kiln.

15. In the clinker burning process, it is essential to maintain kiln charge temperatures in the sintering zone between 1400 and 1500°C to convert the raw meal to clinker. To reach these temperatures, flame temperatures of about 2000°C are necessary. Also, for reasons of clinker quality, excess air is required in the sintering zone to maintain oxidizing conditions. Otherwise, if insufficient oxygen is present, tetracalcium alumino ferrite does not form; instead Fe_2O_3 is reduced to FeO. This leads to a clinker product that produces a quick setting cement with decreased final strength. Additionally, the presence of unburned carbon in the burning region produces a clinker with an undesirable brown colour. (U.S. EPA, 2004)

16. The composition of the clinker, as well as the names and formulas of the clinker components are listed in Table 5. To complete the production of Portland cement, the cooled clinker is ground with a small amount of gypsum or anhydrite. Figure 2 provides a process flow diagram of the general cement manufacturing process.

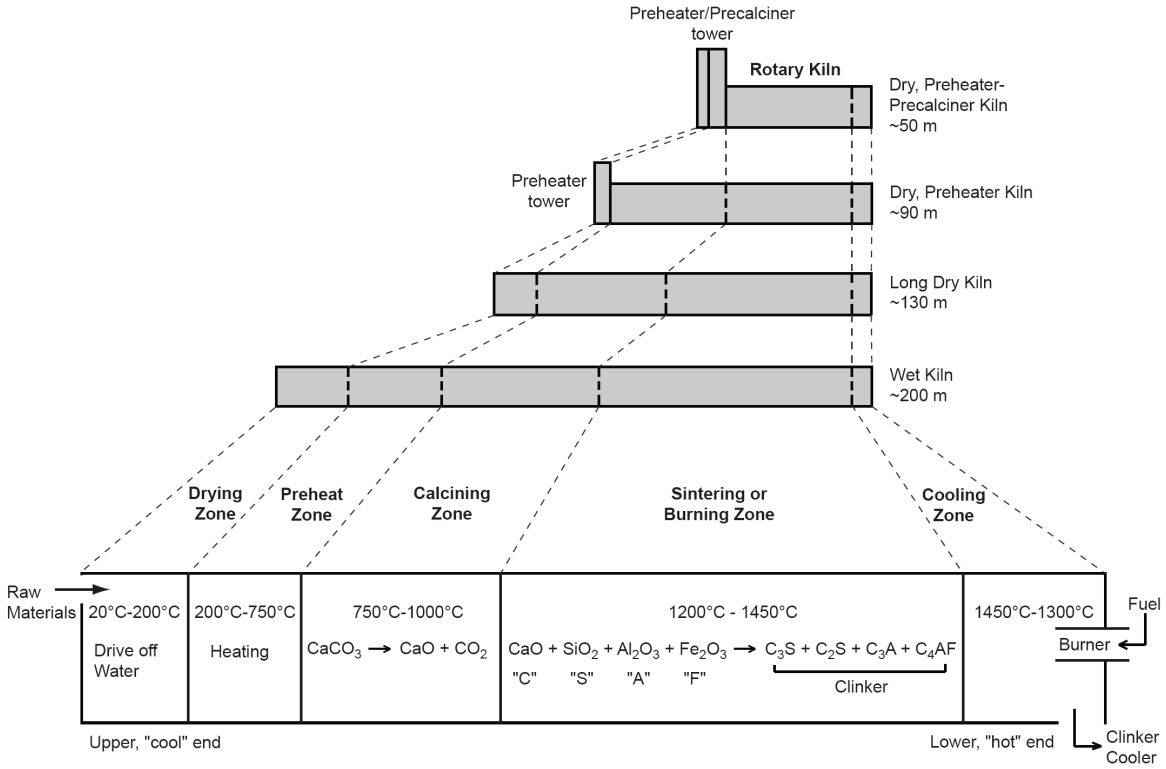
Table 5. Typical mineralogical composition of ordinary Portland cement clinker

Chemical name (common name)	Chemical formula	Common notation a/	Concentration range
Tricalcium silicate ('alite')	Ca_3SiO_5	C_3S	50-70%
Dicalcium silicate ('belite')	Ca_2SiO_4	C_2S	15-30%
Tricalcium aluminate ('aluminate')	$Ca_3Al_2O_6$	C_3A	5-10%
Tetracalcium aluminoferrite ('ferrite')	$Ca_4Al_2Fe_2O_{10}$	C_4AF	5-15%

a/ Abbreviations: C=CaO; S=SiO_2; A=Al_2O_3; F=Fe_2O_3

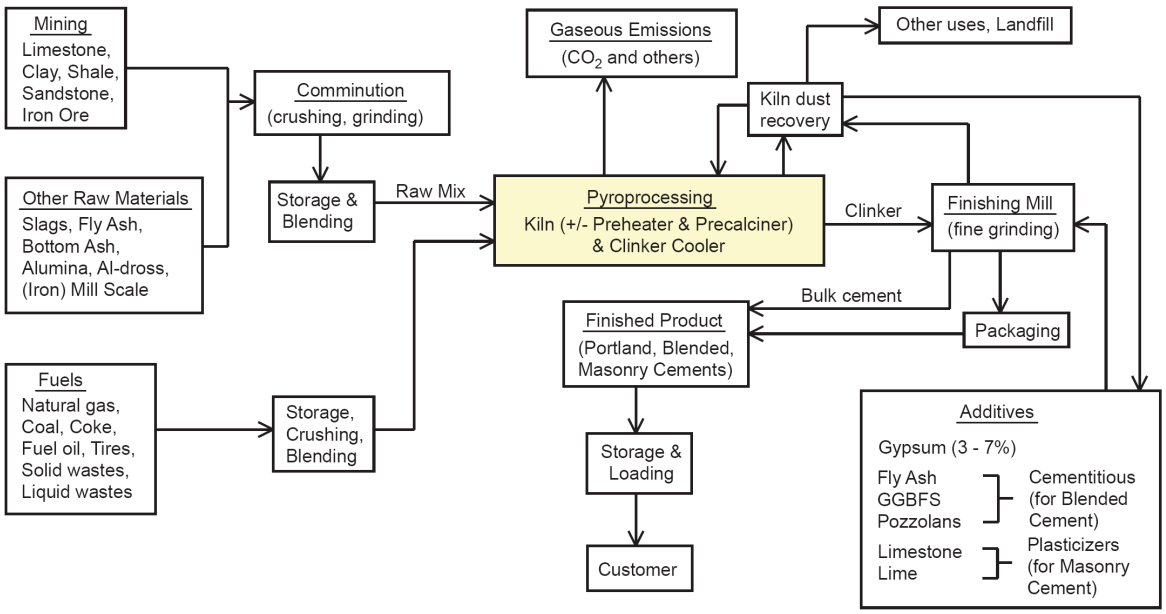
Source: Taylor (1997)

Figure 1. Diagram of 'reaction' zones for different kiln technologies



Source: van Oss (2005)

Figure 2. General cement manufacturing process



Source: van Oss (2005)

Revision date: 1/07/2010

17. Clinker can be made either in energy-intensive and small-scale vertical kilns or in more efficient, larger scale rotary kilns. With the exception of vertical shaft kilns (VSK) still used in certain geographical areas (mainly China and India) (CPCB, 2007; Höhne and Ellermann, 2008), cement clinker is predominantly burnt in rotary kilns. For the manufacture of cement using rotary kilns heating of the raw meal to produce cement clinker can take place in one of four different types of arrangements: the 'dry', 'semi-dry', 'semi-wet', or 'wet' processes (European Commission, 2001; UNEP, 2006):

- Dry process: Dry raw meal is fed to a cyclone preheater or precalciner kiln or, in some cases, to a long dry kiln with internal chain preheater.
- Semi-dry process: Dry raw meal is pelletised with water and fed to a travelling grate preheater prior to the rotary kiln or in some cases, to a long kiln equipped with internal cross preheaters.
- Semi-wet process: Raw slurry is first dewatered in filter presses. The resulting filter cake is either extruded into pellets and fed to a travelling grate preheater or fed directly to a filter cake drier for (dry) raw meal production prior to a preheater/precalciner kiln.
- Wet process: The raw slurry is fed either directly to a long rotary kiln equipped with an internal drying/preheating system (conventional wet process) or to slurry drier prior to a preheater/precalciner kiln (modern wet process).

18. In China approximately 60 percent of the cement was produced in 2005 in VSKs, an amount that is expected to drop to 50 percent by 2015 (Karstensen, 2006a). In Europe, about 78 percent of the cement production is from dry process kilns, a further 16 percent of production is accounted for by semi-dry and semi-wet process kilns, with the remainder of European production, about 6 percent, coming from wet process kilns (European Commission, 2001). In the United States, no new wet kilns have been built since 1975, and approximately 80 percent of U.S. cement production capacity now relies on the dry process technology (U.S. Environmental Protection Agency, 2007). The wet process remains dominant in the former Soviet Union and Australia/New Zealand and is still significant in Canada, India, Latin America and Africa (Watson et al., 2005). Table 6 provides the share mix of kiln technologies in each region or country in 2002.

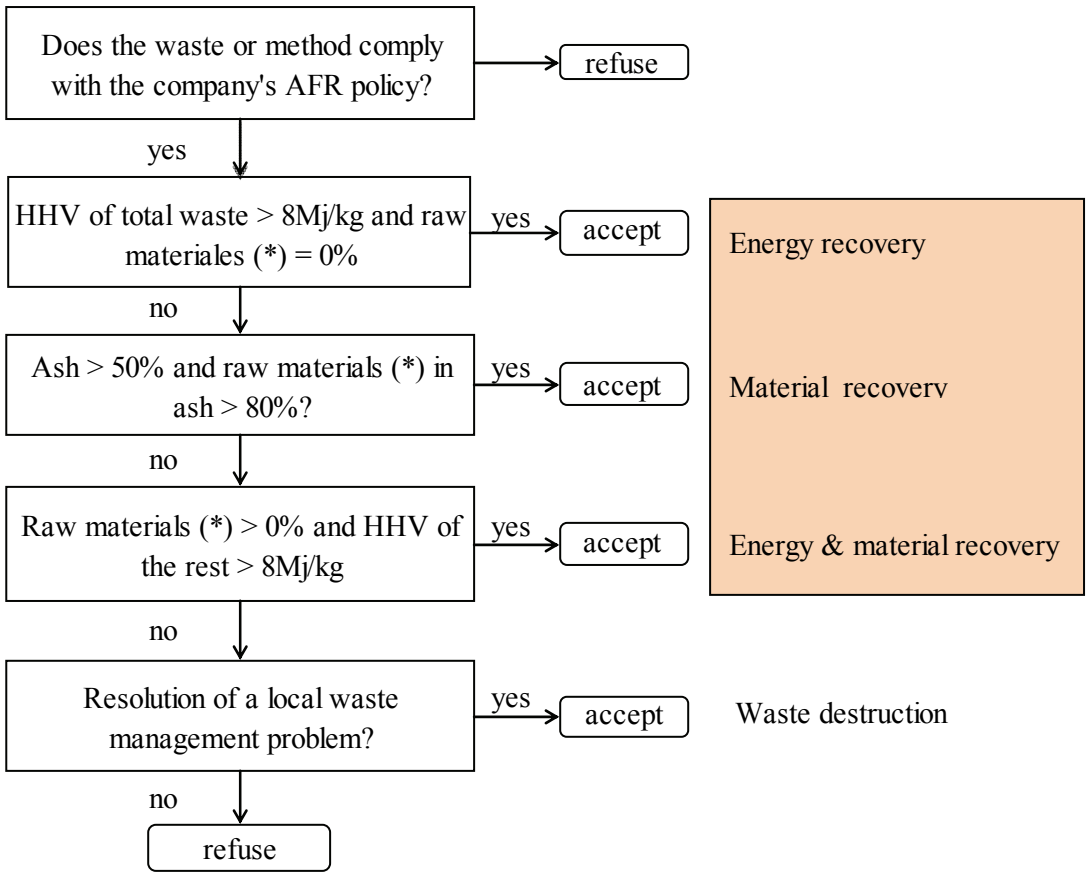
19. Although VSKs are improvements over the old, chimney-type kilns in that some VSKs allow for continuous processing, they are considered to be less energy efficient than the rotary kilns, and VSK clinker (and hence cement) is generally considered to be of lower quality (van Oss, 2005). Furthermore, many VSKs plants have virtually no environmental controls in place, and the nature of the technology precludes effective use of modern dust (and other emission) controls. Compared with preheater/precalciner kilns, VSKs seems to consume from 14 % to 105 % more coal per tonne of clinker; fuel substitution is however not feasible for vertical shaft kilns (Karstensen, 2006a). The raw materials used for cement production in VSKs are exactly the same as in any other production process; corrective materials may also be required to adjust the chemical composition of the raw mix.

Table 6. Share of different kiln types in 2002

Regions, Countries		Kiln Type (% Production)			
		Dry	Semi-Dry	Wet	Vertical
North America	United States	65	2	33	0
	Canada	71	6	23	0
Western Europe		58	23	13	6
Asia	Japan	100	0	0	0
	Australia and New Zealand	24	3	72	0
	China	5	0	2	93
	South East Asia	80	9	10	1
	Republic of Korea	93	0	7	0
	India	50	9	25	16
Eastern Europe	Former Soviet Union	12	3	78	7
	Other Eastern Europe	54	7	39	0
Latin America		67	9	23	1
Africa		66	9	24	0
Middle East		82	3	16	0

Source: Baron et al. (2007)

Annex 2. Example of a Waste Acceptance Decision Chart



HHV: Higher heating (calorific) value
(*) CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3

Source: GTZ/Holcim (2006)

Annex 3. Compilation of Performance Verification and Test Burns Results in Cement Kilns (Karstensen, 2009c)

Introduction

1. Testing of cement kiln emissions for the presence of organic chemicals during the burning of hazardous materials has been undertaken since the 1970s, when the practice of combusting wastes in cement kilns was first considered. Lauber (1987), Ahling (1979) and Benestad (1989) (as cited in Karstensen, 2009c) describe some of these early tests on U.S., Swedish and Norwegian kilns, which confirmed the ability of cement kilns to destroy the organic component of a waste feed. For example, the DRE for chemicals such as methylene chloride, carbon tetrachloride, trichlorobenzene, trichloroethane and PCBs has typically been measured at 99.995 % and better.

2. Comprehensive emission studies have been performed when a conventional fuel such as coal was burned, and when hazardous waste was introduced, and these have generally concluded that no significant differences could be measured between usages of the two fuels. For example, Branscome et al (1985) (as cited in Karstensen, 2009c) observed that "no statistically significant increase in emission rates were observed when the waste fuel (as opposed to coal) was burned". Early studies on dioxin emissions have also come to this conclusion (Branscome et al. (1985), Lauber (1987) and Garg (1990), as cited in Karstensen (2009c)).

Results from trial burns conducted in the 1970s

3. In the mid-1970s, a series of tests were conducted at the St. Lawrence cement plant in Canada to measure the destruction of various chlorinated waste streams being fed into their wet process cement kiln. The overall DRE established for the chlorinated compounds was greater than 99.986 %. This value was considered to be artificially low because the water used to slurry the raw feed was contaminated with low molecular weight chlorinated compounds.

4. In 1978, a series of tests was conducted at the Stora Vika Cement Plant in Sweden to evaluate the efficiency of their wet process cement kiln in destroying various chlorinated waste streams. Although chloroform was found in the stack gas, the majority of the chlorinated compounds were not detected. A DRE greater than 99.995 % was determined for methylene chloride and a DRE greater than 99.9998 % was demonstrated for trichloroethylene.

Results from trial burns conducted in the 1980s

5. Trial burns conducted in the 1980s continued to demonstrate that high DREs could be obtained for the organic constituents in the hazardous waste fuel burned in cement kilns. The results of trial burns of one wet and one dry process cement kiln illustrate the typical values obtained for DREs. The principle organic hazardous constituents selected for the trial burns were methylene chloride, 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), methyl ethyl ketone, 1,1,1-trichloroethane and toluene. As summarized in the table below, the majority of the DREs were greater than 99.99 %. DREs less than 99.99 % resulted from either laboratory contamination problems or improper selection of the POHCs.

Table 1. Average DREs for a wet and a dry process cement kiln

Selected POHCs	Wet process kiln	Dry process kiln
Methylene chloride	99.983 %	99.96 %
Freon 113	>99.999 %	99.999 %
Methyl ethyl ketone	99.988 %	99.998 %
1,1,1-Trichloroethane	99.995 %	>99.999 %
Toluene	99.961 %	99.995 %

Results from trial burns conducted in the 1990s

6. Trial burns conducted in the 1990s have focused on the selection of compounds as POHCs that would not typically be present as contaminants or generated as PICs from the combustion of conventional fuel. Use of this criterion has resulted in more accurate DREs being obtained.

7. In a DRE testing of a dry process cement kiln equipped with a preheater, carbon tetrachloride and trichlorobenzene were chosen as the POHCs. When fed to the burning zone of the kiln, DREs obtained were greater than 99.999 % for carbon tetrachloride and greater than 99.995 % for trichlorobenzene. To determine the limits of the system, DREs were also determined when these POHCs were fed to the kiln inlet (i.e. cool end) of the kiln along with tyres. DREs obtained were greater than 99.999 % for carbon tetrachloride and greater than 99.996 % for trichlorobenzene.

8. DRE testing conducted at a cement kiln owned by United Cement supports the foregoing results. Sulphur hexafluoride was chosen as the POHC because of its thermal stability and ease of measurement in the stack gases. In addition, "contamination" problems and PIC interferences are unlikely with the use of this compound. DREs greater than 99.9998 % were obtained in every case.

9. In 1999 a test burn with pesticide contaminated soil fed into the kiln inlet was performed in a dry process kiln in Colombia. The test burn result showed a DRE of >99.9999 % for all the introduced pesticides.

Results from recent trial burns

10. A test burn with two expired chlorinated insecticide compounds introduced at a rate of 2 tons per hour through the main burner was carried out in Vietnam in 2003. The DRE for the introduced insecticides was >99.99999 %.

11. A three day test burn in Sri Lanka in 2006 demonstrated that the cement kiln was able to destroy PCB in an irreversible and environmental sound manner without causing any new formation of PCDD/PCDF or HCB. The destruction and removal efficiency (DRE) was better than 99.9999% at the highest PCB feeding rate.

12. A five day test burn with POPs contaminated soil was conducted in a cement kiln in Venezuela in 2007. The soil was contaminated with relatively low levels of various chlorinated pesticides, first of all the aldrin, dieldrin and endrin (up to max 551 mg/kg). Measurement showed the same low levels of dieldrin in the stack gas (<0.019 $\mu g/Nm^3$) when no contaminated soil was fed as when feeding 2 tonne/h of contaminated soil containing up to 522 mg dieldrin/kg. It can therefore be assumed that the measured DRE of 99.9994 % achieved with the highest feeding concentration is probably higher in reality.

13. A recent study evaluating more than 2000 PCDD/PCDF cement kiln measurements and indicating that most modern cement kilns co-processing waste (also organic hazardous wastes) can meet an emission level of 0.1 ng PCDD/PCDF I-TEQ/m^3.

Summary

14. Earlier data which indicated cement kiln DRE results below 99.99 % are most probably either from outdated sources or improperly designed tests, or both. In the early years of development of this concept and the sampling and analytical techniques to evaluate its environmental performance, there were several instances where POHCs were selected that did not meet the necessary criteria. For example, a major problem with many early tests was that the POHCs selected for DRE evaluation were organic species that are typically found at trace levels in the stack emissions from cement kilns that burn solely fossil fuel. While these PICs were emitted at very low levels, they nonetheless greatly interfered with the measurement of POHC destruction. Practitioners quickly learned that DRE could not be properly measured if POHCs used in testing were chemically the same or closely related to the type of PICs routinely emitted from raw materials. For that reason, early DRE test results (i.e., before 1990) should always be treated with caution.

15. In some cases however, operational factors during the testing or sampling and analytical techniques contributed to the low DRE results. These typically were problems that occurred only in the earliest tests conducted during the developmental stages of this technology and should be possible to avoid today. Trial burn is a good way of demonstrating a kilns performance and ability to destroy wastes in an irreversible and sound way, but the design and the conditions of the trial is very crucial.

Early applications of trial burn rules to cement kiln evaluation

16. Since the early nineteen seventies, the United States EPA, several state agencies, Canadian, Norwegian, Swedish agencies have conducted studies of the feasibility of using cement kilns for hazardous waste destruction. These wastes have included a broad range of chlorinated hydrocarbons, aromatic compounds, and waste oils. Both wet and dry process cement kilns, aggregate kilns and lime kilns have been used for these tests.

17. The available reports on cement kilns provides data about performance with regard to the following specific compounds: trichloromethane (chloroform); dichloromethane (methylene chloride); carbon tetrachloride; 1,2-dichloroethane; 1,1,1-trichloroethane; trichloroethylene; tetrachloroethylene; 1,1,2-trichloro-1,2,2-trifluorethane (Freon 113); chlorobenzene; benzene; xylene; toluene ; 1,3,5-trimethylbenzene; methyl ethyl ketone; methyl isobutyl ketone; carbon hexafluorine; phenoxy acids; chlorinated hydrocarbons; chlorinated aliphatics; chlorinated aromatics; PCBs; and POPs pesticides.

Table 2. Summary of DREs for selected compounds from the seventies and the eighties

Site	POHC or waste component	DRE
St. Lawrence Cement (Canada)	Chlorinated aliphatics	>99.990
	Chlorinated aromatics	>99.989
	PCBs	>99.986
Stora Vika (Sweden)	Methylene chloride	>99.995
	Trichloroethylene	>99.9998
	All chlorinated hydrocarbons	>99.988
	PCBs	>99.99998
	Chlorinated phenols	>99.99999
	Phenoxy acids	>99.99998
	Freon 113	>99.99986

Site	POHC or waste component	DRE
Brevik (Norway)	PCBs	>99.99999
San Juan Cement (Puerto Rico)	Methylene chloride	93.292-99.997
	Trichloromethane	92.171-99.96
	Carbon tetrachloride	91.043-99.996
Portland (Los Robles)	Methylene chloride	>99.99
	1,1,1-Trichloroethane	99.99
	1,3,5-Trimethylbenzene	>99.95
	Xylene	>99.99
General Portland (Paulding)	Methylene chloride	99.956-99.998
	Freon 113	>99.999
	Methyl ethyl ketone	99.978-99.997
	1,1,1-trichloroethane	99.991-99.999
	Toluene	99.940-99.988
Lone Star Industries (Oglesby)	Methylene chloride	99.90-99.99
	Freon 113	99.999
	Methyl ethyl ketone	99.997-99.999
	1,1,1-trichloroethane	>99.999
	Toluene	99.986-99.998
Marquette Cement (Oglesby)	Methylene chloride	99.85-99.92
	Methyl ethyl ketone	99.96
	1,1,1-trichloroethane	99.60-99.72
	Toluene	99.95-99.97
Rockwell Lime	Methylene chloride	99.9947-99.9995
	Methyl ethyl ketone	99.9992-99.9997
	1,1,1-trichloroethane	99.9955-99.9982
	Trichloroethylene	99.997-99.9999
	Tetrachloroethylene	99.997-99.9999
	Toluene	99.995-99.998
Site I	1,1,1-trichloroethane	99.88-99.98
	Trichloroethylene	99.8-99.994
	Benzene	82.5-98.5
	Tetrachloroethylene	99.87-99.989
	Toluene	99.7-99.90
	Chlorobenzene	99.3-99.4
	Methyl ethyl ketone	99.93-99.98
	Freon 113	99.988-99.998
Site II	Methylene chloride	>99.99996->99.99998
	1,2-dichloroethane	99.91->99.9993
	1,1,1-trichloroethane	99.9998-99.9999
	Carbon tetrachloride	99.8-99.995
	Trichloroethylene	99.996-99.9993
	Benzene	99.75-99.93
	Tetrachloroethylene	99.998-99.9998
	Toluene	99.997-99.9998
	Chlorobenzene	99.92-99.97
	Methyl ethyl ketone	99.996->99.999992
	Freon 113	99.99991-99.99998

Site	POHC or waste component	DRE
Florida Solite Corp.	Methyl ethyl ketone	99.992-99.999
	Methyl isobutyl ketone	99.995-99.999
	Tetrachloroethylene	99.995-99.999
	Toluene	99.998-99.999

Source: EPA (1986) (as cited by Karstensen, 2009c)

18. It should be noted that the DRE calculations did not include corrections for test compounds measured during baseline tests.

19. The issue of PIC formation is one about which there is generally great public concern. Some of the kiln tests demonstrated minor increases in PICs resulting from waste combustion. However, tests run on coal-fired facilities demonstrate that PICs are virtually inevitable for these systems. Although trace quantities (<23 parts per trillion) of polychlorinated dibenzodioxins and dibenzofurans were measured at San Juan during a kiln upset, and trace quantities may have been present at Stora Vika, the EPA summary report concludes that they are not confirmed as PICs from waste production.

20. If waste liquid organic chemicals are fed into the firing end of the cement kiln, it can be readily seen that they will be subject to the high temperatures and long residence times of the cement clinker production process. Consequently, they will be completely destroyed by a combination of pyrolysis and oxidation.

Annex 4. Sources of Air Emissions

Particulate Matter

1. The cement production process includes thermal treatment (drying, heating, calcining, clinkerization, cooling) of materials through direct contact with hot gases. It also includes pneumatic material transports and material classification/separation. At the end of these processes, air/gas and pulverized materials have to be separated. Incomplete separation gives rise to dust emissions (kiln/raw mill main stack, clinker cooler stack, cement mill stacks, material transfer point dedusting air outlets).

2. Outdated air pollution control equipment may emit up to several 100 mg/Nm^3. EPS easily reach < 50 mg/Nm^3. Fabric filters produce values < 20 mg/Nm^3. The visibility limit for point source dust is generally assumed to be around 80 mg/Nm^3.

Sulphur Oxides

3. SO_2 results from the oxidation of sulphide or elemental sulphur contained in the fuel during combustion. In addition, sulphide or elemental sulphur contained in raw materials may be 'roasted' or oxidized to SO_2 in areas of the kiln system where sufficient oxygen is present and the material temperature is in the range of 300-600°C. Sulphates in the raw mix can also be converted to SO_2 through localized reducing conditions in the kiln system.

4. Range of emissions depends on content of volatile sulphur compounds in raw materials. Mostly below 300 mg/Nm^3. Sometimes up to 3000 mg/Nm^3.

Nitrogen Oxides

5. There are four mechanisms of NO_X formation in cement kilns of which thermal and fuel NO_X formation are the most important. Thermal NO_X results from the oxidation of molecular nitrogen in air at high temperature. This phenomenon occurs in and around the flame in the burning zone of a cement kiln at a temperature greater than 1200ºC. Fuel NO_X results from the oxidation of nitrogen in the fuel at any combustion temperature found in the cement process. Because of the lower combustion temperature in the calciner and some sites of supplemental fuel combustion, the formation of fuel NO_X often exceeds that of thermal NO_X at these locations. The generation of feed NO_X has been demonstrated only in the laboratory by heating nitrogen-containing cement raw materials to the range of 300-800ºC in the presence of oxygen. Slow heating, such as occurs in wet and long-dry kilns, appears to increase the yield of NO_X for a given raw material. The yield of feed NO_X is potentially lower when the raw material is heated quickly in a preheater or precalciner system. Prompt NO_X is generated by the reaction of certain fuel-derived radicals with elemental nitrogen in a hydrocarbon flame and is a minor contributor to overall NO_X generation.

6. Range of emissions (unabated) is 300 to 2000 mg/Nm^3.

Carbon Oxides

7. CO is a PIC of carbonaceous fuels resulting from insufficient oxygen at the combustion site, insufficient mixing of oxygen and fuel at the combustion site, and/or rapid cooling of the

combustion products to below the ignition temperature of CO prior to its complete oxidation. CO can be formed unintentionally at any of the combustion sites in the kiln system. The emission of CO usually represents partially burned and under utilized fuel. However, as a result of using oxygen-deficient combustion in the riser duct or calciner as a NO_X control strategy, CO sometimes is generated in the pyroprocess and may appear in the flue gas discharge if it is not somehow oxidized following its formation.

8. CO_2 results from the combustion of carbonaceous fuel and the calcination of the calcareous component of the raw material mix, an essentially unavoidable and fixed consequence of cement manufacture. Of the total amount of CO_2 emitted from a cement kiln, about half of the CO_2 originates from the raw material while the other half originates from the combustion process. There is about one tonne of CO_2 emitted per tonne of clinker produced. More thermally efficient systems emit slightly less than one tonne while less thermally efficient systems emit slightly more than one tonne.

Organic Emissions

9. VOCs are organic compounds that generally contain from one to seven carbon atoms in the respective molecules and are a subset of total hydrocarbons (THCs) emissions from cement kilns. VOC emissions from cement kilns are of interest because of their involvement in the formation of atmospheric ozone and the designation of some VOCs as hazardous air pollutants (HAPs). THCs are primarily generated as a result of evaporation and/or cracking of the constituents of petroleum and kerogens found in the raw material mix. The potential for organic emissions varies with the selection of raw materials and the variability of the concentration of organic constituents within raw material sources. Organic PICs also can be formed as a result of incomplete combustion at any of the combustion sites within a pyroprocessing system.

10. Range of emissions is dependant on content of raw materials of volatile organics. Mostly below 50 mg/Nm^3. Sometimes up to 500 mg/Nm^3.

Acid Gases

11. All the oxidants necessary to convert SO_2 to sulphur trioxide (SO_3) are present in the combustion products of fossil fuel. Therefore, emissions of SO_3 and/or H_2SO_4 mist are a possibility from cement plants. The emissions of H_2SO_4 mist also may increase for those plants employing tailpipe wet scrubbers. The mechanism for the formation of HCl in cement kilns is not fully understood. However, emissions of HCl from cement kilns have been reported over a wide range of values. Perhaps because of the affinity of chlorine for calcium and alkali metals, there is limited evidence that HCl emissions may be independent of chlorine input to a kiln system. Should there be fluorine naturally present in the raw materials or added as a mineralizer, the emission of HF from a cement kiln system is a possibility.

12. Ranges of emissions: SP/PC kiln systems, <10 mg/Nm^3. Wet kilns, up to 80 mg/Nm^3.

Ammonia

13. Trace quantities of NH_3 in the exhaust gas from a cement kiln gas probably result from the pyrolysis of nitrogenous compounds in fossil fuels and raw materials. Ammonia emissions from cement kilns are of primary concern with regard to their potential contribution to regional haze. In

addition, atmospheric reactions occur just outside of the stack between NH_3 and the oxides of sulphur or HCl that produce ammonium sulphate, ammonium bisulphate, or ammonium chloride as very fine particulate matter (PM). These reaction products are observed as the undesirable anomaly known as a 'detached plume'. Depending on the location of the stack observer, the detached plume can give the incorrect appearance of poorly controlled PM emissions from a kiln stack.

14. Range of emissions is <1 to 15 mg/Nm^3 as a rule with exceptions up to 40 mg/Nm^3.

Benzene

15. Benzene might be present in conventional and alternative raw materials and is partially roasted off at material preheating.

16. Range of emissions, normally 1 to 2 mg/Nm^3; up to 3 and more mg/Nm^3 in rare cases

Heavy Metals

17. Heavy metals are ubiquitous in all cement kiln input materials. Since clean gas dust (i.e. dust after the dedusting equipment) is an input materials fraction, it also contains heavy metals. In addition, semi-volatile and volatile heavy metals are evaporated and condense (predominantly) on the fine dust fraction.

18. Most heavy metal emissions (typically 80%) remain below the detection limits. All (with one exception) remain safely below generally adopted limit values. The one exception is mercury, which can exceed limit values in case of excessive inputs with materials. Emission range of mercury is from below detection limit up to < 0.05 mg/Nm^3.

Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

19. Dioxins, furans or advanced precursors might be present in conventional (rarely) and alternative raw materials and are partially roasted off at material preheating. Any chlorine input in the presence of organic material may potentially cause the formation of PCDD and PCDF in heat (combustion) processes. PCDD/PCDF can be formed by the de novo synthesis mechanism in or after the preheater and in the air pollution control device if chlorine and hydrocarbon precursors are available in sufficient quantities in the temperature range 200º C to 450º C.

20. A comprehensive survey of PCDD/PCDF emissions from cement kilns in developed and developing countries is given in a report by Karstensen (2006b).

21. In a survey performed by Cembureau, PCDD and PCDF measurements from 110 cement kilns in 10 countries were presented. The countries covered by the survey were Czech Republic, Denmark, France, Germany, Hungary, Italy, the Netherlands, Norway, Spain and the United Kingdom. The average concentration, taking into account all of the data in this dataset, was 0.016 ng I-TEQ/m^3. The range between the lowest and highest concentrations measured was < 0.001 to 0.163 ng I-TEQ/m^3. All measurements were expressed corrected to standard conditions (dry gas, 273 K, 101.3 kPa and 10% O_2).

22. A report from the Holcim Cement Company, which operates cement kilns worldwide, gives average PCDD/PCDF values for 2001 and 2002 as 0.041 ng TEQ/Nm^3 (71 kilns) and 0.030 ng TEQ/Nm^3 (82 kilns) respectively. Of these measurements, 120 were from countries within the

Organisation for Economic Co-operation and Development (OECD), with an average value of 0.0307 ng TEQ/Nm3; the minimum and maximum values measured were 0.0001 and 0.292 ng TEQ/Nm3 respectively, with nine long wet kilns being above 0.1 ng TEQ/Nm3. For the 29 measurements from non-OECD countries, the average value was 0.0146 ng TEQ/Nm3; the minimum and maximum values measured were 0.0002 and 0.074 ng TEQ/Nm3 respectively, with no measurements being above 0.1 ng TEQ/Nm^3.

23. The PCDD/PCDF data presented by Karstensen (2006b) shows that:

- Most cement kilns can meet an emission level of 0.1 ng TEQ/Nm^3 if primary measures are applied;
- Co-processing of AFR, fed to the main burner, kiln inlet or the precalciner does not seem to influence or change the emissions of POPs;
- Data from dry preheater and precalciner cement kilns in developing countries show emission levels much lower than 0.1 ng TEQ/Nm^3.

Polychlorinated Biphenyls and Hexachlorobenzene

24. Hexachlorobenzene (HCB) and PCB have not been the subject of regulatory monitoring in cement plants to date. Most measurements that have taken place have not detected HCB emissions. As regards PCB emissions, 40 measurements carried out in 13 kilns in Germany in 2001 revealed a maximum concentration of 0.4 µg PCB /Nm^3; in nine of the 40 measurements, no PCB were detected. From Vietnam co-processing of pesticides has shown emissions of dioxin like PCB of 0.001 ng TEQ/m^3 and HCB emissions below the detection limit of 31 ng/m^3.

Sources: GTZ/Holcim (2006), UNEP (2007), Karstensen (2006b), Greer (2003)

Annex 5. Example Emission Limit Values for Cement Kilns Co-processing Hazardous Waste (Department for Environmental Affairs and Tourism, Republic of South Africa, 2009)

Emissions	Air emission standard (a)	
PM (Total particulate matter)	30 (b)	80 (c)
TOC	10 (d)	
HCl	10	
HF	1	
SO_2	50 (d)	
NO_X	500 (e)	800 (f)
Hg	0,05	
Cd, Tl (Sum total)	0,05	
Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V (Sum total)	0,5	
PCDD/PCDF (ng/Nm^3 1-TEQ)	0,1	

(a) Concentration expressed as mg/Nm^3 (daily average) unless otherwise stated, and at normalized conditions of 10% O_2, 101 kPa 273K/ 0ºC, dry gas

(b) PM limit for new kilns co-processing AFR

(c) PM limit for existing kilns co-processing AFR (excluding POPs waste), provided that current particulate emissions (as established through baseline monitoring) are not increased by the introduction of AFR

(d) Limits for TOC or SO_2 do not apply where elevated emissions result from conventional fuels or raw material, i.e. not from the co-processing of AFR provided that current TOC and SO_2 emissions (as established through baseline monitoring) are not exceeded the introduction of AFR.

(e) NOx limit for new kilns co-processing AFR

(f) NOx limit for existing kilns co-processing AFR (excluding POPs waste), provided that current NOx emissions (as established through baseline monitoring) are not increased by the introduction of AFR.

1. All emission monitoring results must be reported as a daily average concentration expressed as mg/Nm^3, or ng/Nm^3 1-TEQ for PCDD/PCDF, and at normalized conditions of 10% O_2, 101,3 kPa, 273 K, dry gas

2. Exit gas temperatures must be maintained below 200 ºC if applicable

3. Pollution control devices (exhaust gas cooling and bag filter or ESP) must have a daily availability of 98% (i.e. maximum downtime of 2% or 30 minutes per running 24 hours). The cumulative annual downtime (total downtime over one year period) may however not exceed 60 hours (0,685 % per annum)

4. Continuous, on-line measurement of the following emissions and operating parameters is required: Particulate matter (total particulate); O_2; CO; NO_X; SO_2; HCl; HF; VOC/TOC; emission exhaust volume (e.g. Nm^3/h) and flow rate (e.g. m/s); water vapour content of exhaust gas (humidity); exhaust gas temperature; internal process temperature(s); pressure; and availability of air pollution control equipment (exit gas cooling and ESP/bag filter)

5. Appropriate installation and functioning of automated, continuous, monitoring equipment for emissions to air; which are subject to quality control and to annual surveillance test. Independent calibration by means of parallel measurements with the reference methods at least every three years.

6. Periodic measurements of heavy metals and dioxin and furan emissions (bi-annual) by independent/external, accredited specialist during the first 12 months of AFR co-processing, and annually thereafter.

7. Average emission values for heavy metals to be measured over a minimum sample period of 8 hours, and average values for dioxins and furans (expressed as 1-TEQ) over a sample period of a minimum of 6 hours and a maximum of 8 hours.

8. Periodic measurements of air emissions to be carried out representatively to provide accurate and scientifically corrected emission data and results, and sampling and analysis must be carried out by independent accredited laboratories.

9. To ensure valid monitoring results are obtained, no more than five half-hourly average values in a day, and no more than ten daily average values per year; may be discarded due to malfunction or maintenance of the continuous measurement system.

10. Treatment of High Level POPs Containing Waste (as defined by the Stockholm and Basel Conventions) are to be preceded by an independently monitored Performance Verification Test to determine the DE and DRE of principal organic hazardous compounds (PHC); using a suitable verification compound (e.g. trichloroethane).

11. A detailed, independent report documenting and interpreting the results of the Performance Verification Test must be compiled. As a minimum a DE/DRE of 99.9999% would be required, as well as compliance with Air Emission Standards.

STEAM REFORMING OF ETHANOL OVER SOL-GEL-SYNTHESIZED MIXED OXIDE CATALYSTS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
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BY

HAKAN ÖNDER OLCAY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

JULY 2005

Approval of the Graduate School of Natural and Applied Sciences

_____

Prof. Dr. Canan ÖZGEN

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

_____

Prof. Dr. Nurcan BAÇ

Head of Department

This is to certify that I have read this thesis and that in my opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science

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ABSTRACT

STEAM REFORMING OF ETHANOL
OVER SOL-GEL-SYNTHESIZED MIXED OXIDE CATALYSTS

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Depletion in the reserves of fossil fuels, inefficient energy production from these fuels and the negative effect of their usage on atmosphere, and thereby, on human health have accelerated researches on clean energy. Hydrogen produced from ethanol when used in fuel cells not only generates efficient energy but also creates a closed carbon cycle in nature.

ZnO and Cu/ZnO catalysts are known with their superior performance in alcohol synthesis. From the principle of microkinetic reversibility they are expected to be superior catalysts for the steam reforming reaction of ethanol as well. ZnO catalysts can be modified by precious, Pd, or non-precious, Cu, metals to enhance hydrogen desorption capability, and dispersed on SiO_2 for high surface areas via sol-gel technique.

Steam reforming tests over ZnO catalysts revealed that they act only as ethanol dehydrogenation catalysts in the temperature range of 300-500°C. Promotion with Pd or Cu decreased hydrogen selectivity due most probably to unreachable closed pores of the catalysts. Autothermal reforming tests over both ZnO/SiO_2

and Co/SBA-15 catalysts, on the other hand, gave rise to the formation of several side products.

Keywords: Ethanol Steam Reforming, Palladium, Copper, Zinc Oxide, Cobalt

ÖZ

SOL-JEL İLE HAZIRLANMIŞ KARIŞIK OKSİT KATALİZÖRLER ÜZERİNDE ETANOLÜN BUHAR RİFORMLAMASI

Olcay, Hakan Önder
Yüksek Lisans, Kimya Mühendisliği Bölümü
Tez Yöneticisi : Prof. Dr. Deniz Üner

Temmuz 2005, 91 sayfa

Fosil yakıt yataklarındaki azalma, bu yakıtlardan elde edilen enerjinin verimsiz oluşu, ve bunların kullanımının atmosfer ve insan sağlığı üzerindeki olumsuz etkisi temiz enerji konulu araştırmalara ivme kazandırmıştır. Etanolden üretilen hidrojen yakıt hücrelerinde kullanıldığında hem verimli enerji üretilmekte hem de doğada kapalı bir karbon çevrimi oluşturulmaktadır.

ZnO ve Cu/ZnO katalizörler alkol sentezlemedeki üstün performanslarıyla bilinirler. Mikrokinetik tersinirlik prensibine dayanarak bu katalizörlerin etanol buhar riformlaması tepkimesinde de etkin rol oynayacağı düşünülmektedir. Sol-jel tekniğiyle ZnO katalizörlerin hidrojen dezorplama yeteneğini artırmak amacıyla Pd gibi değerli metallerle veya Cu gibi değerli olmayan metallerle yapısı değiştirilebilir, ve bu katalizörler yüksek yüzey alanı sağlama amacıyla SiO_2 üzerine dağıtılabilir.

ZnO katalizörler üzerinde 300-500°C sıcaklıklarda gerçekleştirilen buhar riformlaması deneyleri bu katalizörlerin sadece etanolden hidrojen koparmaya yardımcı olduğunu göstermiştir. Pd veya Cu eklenmiş katalizörlerde yapılarında bulunan olası kapalı gözeneklerin bir sonucu olarak daha az hidrojen seçiciliği

elde edilmiştir. ZnO/SiO_2 ve Co/SBA-15 katalizörler üzerinde oksijen ortamında gerçekleştirilen düzeltim deneylerinde ise bir dizi yan ürün dağılımı elde edilmiştir.

Anahtar Kelimeler: Etanol buhar riformlaması, Paladyum, Bakır, Çinko oksit, Kobalt

To My Grandma

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CHAPTER 1

INTRODUCTION

World's energy consumption depends largely on fossil fuels. More than 85% of energy consumed in the last decade was obtained from fossil fuels [1]. Figure 1 illustrates the world primary energy consumption by energy source for years 1970-2001 and with predictions up to 2025.

In 1956 M. King Hubbert, a geologist with Shell Oil, observed that unrestrained extraction of a finite resource rises along a bell-shaped curve which gives peak when about half the resource is gone. Based on his theory, by 2060s petroleum will be exhausted [3]. Today there is still an increasing demand for oil the widespread usage of which in the transportation sector contributes to serious environmental problems. As an immediate precaution automobile industry has put into operation the usage of catalytic converters on both gasoline-fueled and diesel-fueled engines, and particulate filters on diesel-fueled engines which helped the emission values to decrease in one automobile; however, total emission values continued to increase upon increasing demand [1,4]. Figure 2 illustrates world energy-related carbon dioxide emissions by fuel type from 1970 to 2001, and also presents predictions until 2025 if no further precautions are taken. According to Kyoto Protocol signed in 1997 many countries agreed on reducing their overall emissions of six greenhouse gases (CO_2, CH_4, N_2O, HFCs, PFCs and SF_6) by at least 5% below 1990 levels over the period between 2008 and 2012 [5].

Both decrease in fossil fuel reserves and new regulations on emission control lead the way to the development of new engines and alternative fuels like

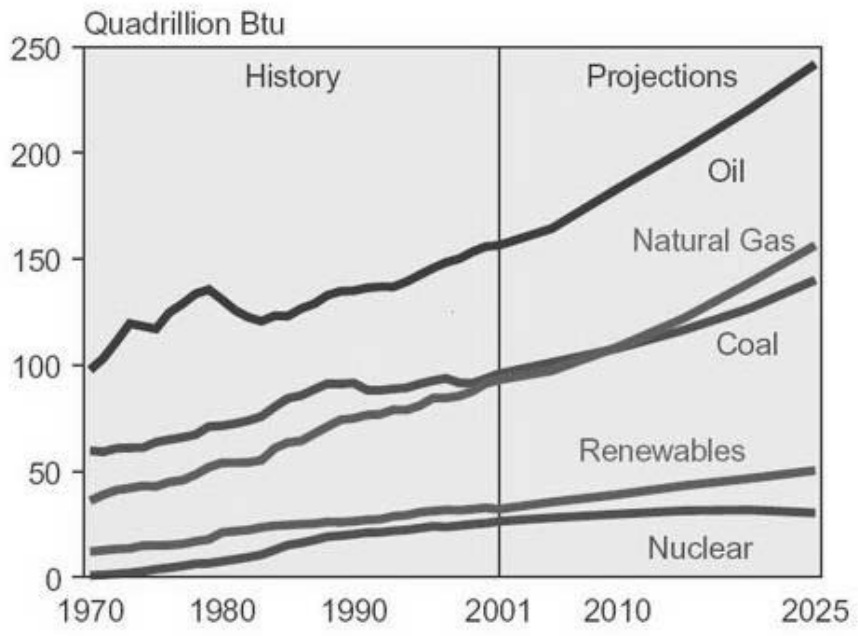

Figure 1. *World primary energy consumption by energy source [1,2]*

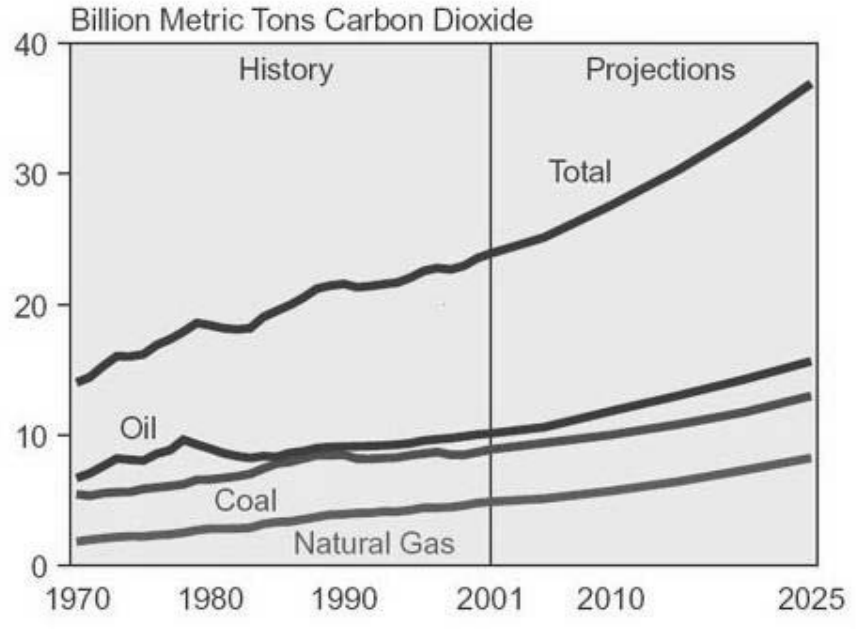

Figure 2. *World energy-related carbon dioxide emissions by fuel type [1,2]*

hydrogen. Hydrogen can be derived from carbonaceous materials, e.g. hydrocarbons, and/or water through electrolysis, steam reforming, thermal dissociation or partial oxidation [6]. Biomass gasification or reforming arose as new areas of research.

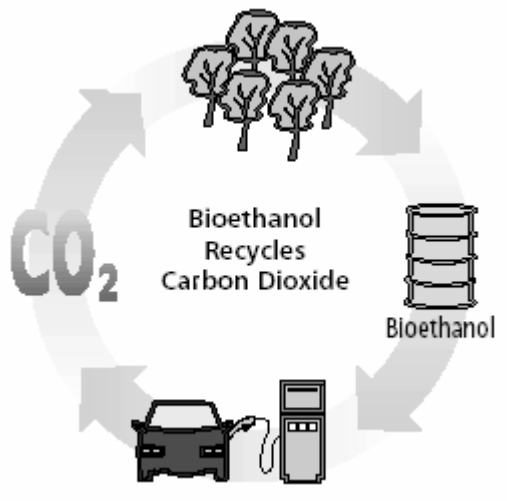

Figure 3. *Closed carbon cycle [8]*

Sugar, starch, oils and crop wastes have been used as biomasses for hydrogen generation; however, their usage has been limited either by low hydrogen selectivities or by their high costs [7]. Ethanol is now another candidate. Hydrogen produced from especially bioethanol[1] when used in fuel cells for electricity generation creates a closed carbon cycle in nature releasing no additional carbon dioxide [8]. This closed carbon cycle is illustrated in Figure 3.

[1] Bioethanol is an aqueous solution containing ca. 12wt% ethanol.

Hydrogen can be produced from ethanol either by steam reforming or by direct partial oxidation:

$$C_2H_5OH + H_2O \leftrightarrow 2CO + 4H_2 \qquad \Delta H_R^o = +256\,kJ/mol \tag{1}$$

$$C_2H_5OH + \tfrac{1}{2}O_2 \leftrightarrow 2CO + 3H_2 \qquad \Delta H_R^o = +14\,kJ/mol \tag{2}$$

These reactions are followed by water-gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_R^o = -41\,kJ/mol \tag{3}$$

Heat needs to be supplied either externally or internally to the system as both of the reactions (1) and (2) are endothermic. Therefore, partial oxidation reaction cannot take place without some external heat or without some total oxidation:

$$C_2H_5OH + 3O_2 \leftrightarrow 2CO_2 + 3H_2O \qquad \Delta H_R^o = -1277\,kJ/mol \tag{4}$$

Heat generated by total oxidation reaction can also be used for steam reforming case. This time a combination of steam reforming reaction with partial and total oxidation reactions are under consideration along with the water-gas shift reaction:

$$C_2H_5OH + 2H_2O + \tfrac{1}{2}O_2 \leftrightarrow 2CO_2 + 5H_2 \qquad \Delta H_R^o = -68\,kJ/mol \tag{5}$$

This reaction is named as indirect partial oxidation or autothermal reaction [7,9].

In this study, sol-gel-synthesized supported zinc oxide and cobalt catalysts were tested for their activities and selectivities towards hydrogen in ethanol steam reforming and autothermal reforming.

Deluga et al. [7] have presented a simple economic analysis of autothermal ethanol reforming for producing hydrogen for fuel cells. They considered a

totally idealized cycle starting from formation of glucose by photosynthesis and ending up in a fuel cell through ethanol fermentation from glucose and autothermal reforming of ethanol. They carried out the analysis taking only the reaction enthalpies into account. Assuming an ethanol cost of $1 per gallon, they arrived at a fuel cost of $0.04 per kWh. This value also applies for ethanol steam reforming as this idealized system consists of same species for both reforming cases.

An economic analysis similar to that of Deluga et al. [7], however, that rely on a more realistic model was also carried out in this study. A fuel cost of $0.09 per kWh was obtained at the end for both steam reforming and autothermal reforming cases. This value in fact decreases the annual fuel cost of a gasoline vehicle by more than a factor of two when compared with a hydrogen fuel cell vehicle [10]. Details of this analysis are given in Appendix A.

The next chapter, Chapter 2, reviews the literature about studies on hydrogen production from alcohols as well as on alcohol synthesis. Thermodynamics of alcohol-water systems were also discussed in that chapter. Chapter 3, on the other hand, describes the details of the experimental work carried out. Results of this work are given in Chapter 4 along with comments and discussions. Following two chapters, Chapters 5 and 6, lastly summarizes and arrives at conclusions, and gives some recommendations, respectively.

CHAPTER 2

LITERATURE SURVEY

Besides being a biomass, ethanol is an alcohol. Reverse of the ethanol steam reforming reaction (Reaction (1)) is nothing but ethanol synthesis from syngas. Therefore, starting literature survey with alcohol synthesis studies would be very well appropriate. In the second part, studies on reaction thermodynamics of ethanol-water systems will be explained. The rest of this chapter will be on various papers dealing with steam reforming of ethanol and methanol, and possible side reactions.

2.1. Lower and Higher Alcohol Synthesis

Catalysts are substances that change the reaction rate by promoting a different mechanism for the reaction without being consumed in the reaction. As they decrease the activation energy barrier of the reaction, from the principle of microkinetic reversibility, they also decrease the activation energy barrier for the reverse of that reaction. In this respect, it may be expected for a good higher alcohol synthesis catalyst also to be a good steam reforming catalyst.

Claus et al. [11] listed the routes for ethanol synthesis available in literature. According to their analysis, there are mainly four economically attractive routes to ethanol:

1. Ethylene hydration: $C_2H_4 + H_2O \leftrightarrow C_2H_5OH$
2. Hydrocarbonylation of methanol: $CH_3OH + CO + H_2O \leftrightarrow C_2H_5OH + O_2$
3. Synthesis from syngas: $CO + 2H_2 \leftrightarrow CH_3OH$

4. Hydrogenolysis of acetate

It is known that acetate production takes place in two steps:

- Methanol carbonylation to acetic acid: $CH_3OH + CO \leftrightarrow CH_3COOH$
- Esterification of acetic acid with methanol or ethanol:
  $CH_3COOH + CH_3OH \leftrightarrow CH_3COOCH_3 + H_2O$ or,
  $CH_3COOH + CH_3CH_2OH \leftrightarrow CH_3C(O)OCH_2CH_3 + H_2O$

Claus et al. have studied the selective hydrogenolysis of methyl and ethyl acetate to ethanol over different copper-based and supported Group VIII metal (Pd, Rh, Pt, Co, Ni) catalysts (CuO/MgO-SiO_2, CuO/ZnO/Fe_2O_3, CuO/ZnO, CuO/Al_2O_3-SiO_2, CuO/ZnO/MnO/Al_2O_3, Co/TiO_2, Co-Rh/TiO_2, Co-Rh-Fe/TiO_2, Co-Rh-Cu/TiO_2, Ni/SiO_2, Pd/Al_2O_3, Zn-Pd/Al_2O_3, Rh on activated carbon, Rh/Al_2O_3, Pt/Al_2O_3, Co/TiO_2, Co-Rh-Cu/TiO_2) in the gas phase at 448-623 K and 0.1-6.0 MPa. Over copper catalysts, they proposed the following reaction mechanism to take place:

I. $CH_3COOCH_3 + 2H_2 \leftrightarrow CH_3CH_2OH + CH_3OH$

II. $CH_3COOCH_3 + CH_3CH_2OH \leftrightarrow CH_3COOCH_2CH_3 + CH_3OH$

III. $CH_3COOCH_2CH_3 + H_2 \leftrightarrow C_2H_4O + CH_3CH_2OH$

IV. $C_2H_4O + H_2 \leftrightarrow CH_3CH_2OH$

Product distribution for Cu catalysts contains ethanol, methanol, ethyl acetate and above 260°C, methane and ethane. It is the CuO/MgO-SiO_2 catalyst showing the best result in ethanol synthesis as the basic MgO helps creation of electron-rich copper sites.

Addition of Fe and Mn to the catalysts promotes ethanol synthesis changing the side product distribution a little bit. For instance, over iron-promoted

$CuO/ZnO/MnO/Al_2O_3$ catalyst, acetaldehyde, 2-butanone, butanal, butanol, butyl acetate and acetone were obtained.

Bimetallic catalysts and all Cu catalysts except CuO/Al_2O_3-SiO_2, which showed deactivation above 260°C, exhibit high activity and selectivity (98%). Increase of temperature and pressure also promoted the ethanol and methanol selectivities.

From the kinetics point of view, comparison of turnover frequencies showed that acetaldehyde is more rapidly hydrogenated. Also, hydrogenolysis of ethyl acetate proceeds faster than that of methyl acetate. It is further shown that over CuO/MgO-SiO_2 catalyst reaction orders with respect to methyl acetate and hydrogen (Reaction I in the above mechanism), methyl acetate and ethanol (II), and ethyl acetate and hydrogen (III and IV) are all equal to one.

Product distributions obtained over Group VIIIB metal catalysts are summarized in Table 1 below.

Table 1. *Product distributions obtained for methyl acetate hydrogenolysis over Group VIIIB metal catalysts of the study by Claus et al. [11]*

Catalyst	**Product Distribution**
Ni/SiO_2	Methane, ethane, CO_x, acetic acid
Pd/Al_2O_3	Ethyl acetate
Zn-Pd/Al_2O_3	Ethanol
Rh/Activated Carbon	Acetic acid, methane, ethane
Rh/Al_2O_3	Methane, ethane, acetic acid, ethanol, ethyl formate, diethyl ether
Pt/Al_2O_3	Ethanol, ethane, diethyl ether

No activity was observed on Pd/Al_2O_3 whereas over monometallic catalysts comprising Rh, Pt and Ni, the hydrogenolysis of ethyl acetate is a nonselective reaction. As a note, formation of diethyl ether over alumina supported catalysts results from alcohol dehydration on acidic alumina.

Finally, Co/TiO_2 catalyst exhibited high activity and selectivity towards ethanol. Addition of Rh decreases selectivity due to formation of oxygenates; however, further addition of Fe increased ethyl acetate conversion. On the other hand, $Co-Rh-Cu/TiO_2$ performed poor results.

Nunan et al. [12,13] have investigated the effect of Cs/Cu/ZnO and $Cs/Cu/ZnO/Me_2O_3$ catalysts (Me = Cr, Al, Ga) with different Cs amounts on higher alcohol synthesis at 583 K, 7.6 MPa and with $H_2/CO = 0.45$ synthesis gas at GHSV = 5330 liters (STP)/kg cat/h.

Alumina and chromia are commercial supports because all practical industrial methanol synthesis catalysts are supported with alumina and chromia. They increase the surface area and stability of the catalyst, and therefore, they are structural promoters. They also induce the formation of side products like dimethyl ester (which can also be inhibited by Cs doping) and hydrocarbons.

Addition of cesium promotes methanol synthesis and water-gas shift reaction, as well as, the formation of ethanol and methyl formate. Alumina causes occlusion of cesium by burying cesium into bulk so that C-C bonds cannot be made. As a result over alumina supported cesium catalysts methanol is synthesized as the only major alcohol. On the other hand, presence of alumina support promotes total alcohol selectivity (for the case of Cs doped catalysts, in other words, methanol selectivity). Chromia, alternatively, promotes especially higher alcohol synthesis bearing no effect on the mechanism. When Cs is doped on the chromia supported catalyst, selectivities to branched alcohols like 1-propanal, 2-methyl-1-propanol, 2-methyl-1-butanol are affected.

Effect of cesium on higher alcohol synthesis mechanism was probed by ^{13}C nuclear magnetic resonance (NMR) analysis. Results showed that over Cu/ZnO catalysts higher alcohols are synthesized by linear insertion chain growth,

$$CH_3{}^{13}CH_2OH \xrightarrow{CO/H_2} CH_3{}^{13}CH_2CH_2OH \quad (6)$$

whereas, over Cs/Cu/ZnO catalysts it is the β-carbon addition, which is also named as aldol coupling with oxygen retention reversal,

$$CH_3{}^{13}CH_2OH \xrightarrow{CO/H_2} {}^{13}CH_3CH_2CH_2OH \quad (7)$$

Cu/ZnO is a hydrogenation catalyst. Doping of cesium provides basic sites which prevents production of side products, which helps promoting higher alcohol synthesis. On the other hand, cesium blocks hydrogenation sites on the catalyst surface. Therefore, higher alcohol selectivity passes through a maximum as amount of cesium on the catalyst increases due to this bifunctional nature of the catalyst. Similarly, chromia has an acidic nature which promotes higher alcohol synthesis, and ester production (Klier et al. [14]). However, in order to prevent formation of side product which are also promoted by this acidity, Cs should be doped to bring some basicity.

Finally, product distribution obtained both over Cs/Cu/ZnO and Cs/Cu/ZnO/Cr_2O_3 are similar. Cs/Cu/ZnO/Ga_2O_3 is a poor methanol catalyst because Ga interacts with Cs.

Smith et al. [15] have developed a kinetic reaction network for the synthesis of oxygenates over Cs-promoted Cu/ZnO catalysts in a differential reaction regime. According to previous studies there are basically three mechanistic reaction paths for higher alcohol synthesis over Cs/Cu/ZnO that are dominant:

- Insertion of CO or a single-carbon (C_1) intermediate to yield linear alcohols (l)
- β-addition yielding 2-methyl-branched primary alcohols (β)
- Methyl ester formation by oxygen attachment of a C1 intermediate to the α-carbon of the lower alcohol (α)

These three reaction paths are illustrated in Figure 4.

Estimates of the kinetic parameters showed that the β-addition is faster than linear growth, which results in high selectivities to branched alcohols like 2-methyl-1-propanol. It was also found that the rate of growth of double-carbon (C_2) intermediate is faster than for any other C_n ($n \geq 2$) intermediate, which is specific to Cs-promoted catalyst.

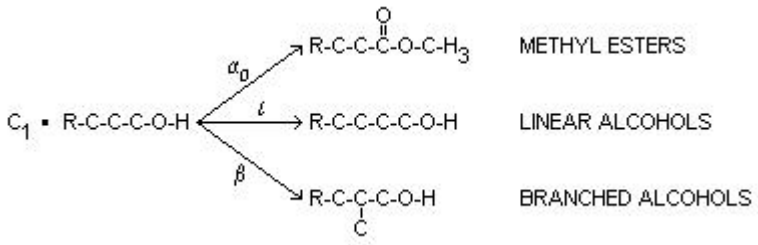

Figure 4. *Dominant mechanisms in higher alcohol synthesis*

Klier et al. [14] have also used Cs-promoted catalysts for higher alcohol synthesis. They used a double-bed reactor packed with $Cs/Cu/ZnO/Cr_2O_3$ and high temperature $Cs/ZnO/Cr_2O_3$ catalysts and sent hydrogen-deficient syngas. Main products obtained were isobutanol and methanol.

They have also tested other catalysts in this dual-bed reactor system. Over SO_4^{2-}/ZrO_2 and H-mordenite, a product distribution including butane, methyl-isobutyl ether (MIBE), methyl-tertiarybutyl ether (MTBE) (minor) and dimetyl ether was obtained. Using Amberlyst-15 instead of H-mordenite resulted in an increase in the selectivity of MTBE. MTBE is known to be an octane enhancer; whereas, MIBE is a potential cetane booster.

Ehwald et al. [16] have tested silica supported Rh, Rh-Mn-Li, Rh-Ir-Mn-Li, Rh-Mn-Li-Cu-Zn and Cu-Zn catalysts, and some mixtures of these catalysts for ethanol synthesis. It is known that rhodium catalysts especially when promoted by elements like iron, manganese and molybdenum exhibit high selectivities towards C_2-oxygenates. The reasons of those high selectivities can be attributed to the promoter's ability,

- to create new active sites with direct interaction of CO oxygen with the promoter cation,
- to create new active sites for the activation of hydrogen (as in the case of Mo),
- to stabilize positive oxidation states of rhodium by electronic interaction.

Previous studies showed that addition of Fe to $Rh\text{-}Ir/SiO_2$ catalyst helps converting the primary product, acetaldehyde, into ethanol.

Copper catalysts are known to be active for hydrogenation of acetaldehyde to ethanol and for hydrogenolysis of aliphatic acetates to ethanol and their corresponding alcohols. Rh/SiO_2 catalyst produces hydrocarbons, methanol, ethanol and acetaldehyde. Addition of Mn and Li (over $Rh\text{-}Mn\text{-}Li/SiO_2$) changes the product distribution as ethanol, acetaldehyde and acetic acid. Therefore, further addition of $CuO\text{-}ZnO\text{-}SiO_2$ as a second component to the promoted Rh catalyst results in an increase in both activity and ethanol selectivity as in the other two-component systems.

Rh-Mn-Li catalyst shows better results in terms of activity when compared to Rh-Ir-Mn-Li catalyst. This is because presence of Ir causes formation of a surface alloy destructing the rhodium ensembles on the surface which are necessary for hydrocarbon formation. On the other hand, Li reduces the hydrogenation ability of the catalyst. Yet, compared to these catalysts, poorer result was obtained with CuO-ZnO catalyst.

Transmission electron micrographs have shown that effects of promoters are not due to a particle size difference. This is because particle sizes do not differ from each other much.

Increase in pressure promoted the selectivities for methanol, ethanol and other oxygenates. Increase in temperature, alternatively, increased methane selectivity.

Rh-Mn-Li-Cu-Zn/SiO_2 catalyst was the poorest catalyst among all as Zn was inhibiting the activity of Rh for CO hydrogenation while Cu was decorating the active Rh sites.

2.2. Reaction Thermodynamics of Ethanol-Water Systems

The thermodynamic feasibility of ethanol steam reforming has been examined by various studies [17,18,19]. Effects of operational parameters on equilibrium composition can be identified either by stoichiometric thermodynamic approach (STA) or by nonstoichiometric thermodynamic approach (NSTA) [19]. In NSTA, the equilibrium composition of the system is found by direct minimization of the Gibbs free energy for a given set of species without specifying any possible reactions. In STA, on the other hand, the system is described by a set of stoichiometrically independent reactions. Major drawback of STA is that such *arbitrarily* chosen chemical reactions may lead to erroneous results. To eliminate the potential of arriving at such flawed conclusions, Fishtik et al. [19] have introduced the concept of what they call as response reactions (RERs). In their study, they have transformed their arbitrary set of

stoichiometrically independent reactions to be used in STA into response reactions which are unique, and thus, independent of the initial choice of that set of reactions.

Vasudeva et al. [18] used NSTA considering nine species at equilibrium: Ethanol, *acetaldehyde*, methane, carbon monoxide, carbon dioxide, hydrogen, water, *ethylene* and *elemental carbon*. They also carried out calculations considering six of those species excluding the ones written above in an italic fashion to be comparable with the work done by Garcia and Laborde [17]. Results showed that hydrogen formation is favored at high temperatures with low concentrations of water, and at low temperatures with high water concentrations. On the other hand, they have also observed that high water amount in the feed reduces both the carbon monoxide amount and the amount of elemental carbon produced per ethanol. Temperature, however, plays differently, favoring carbon monoxide at high temperatures, and elemental carbon at low temperatures.

Fishtik et al. [19] also made use of NSTA and obtained a distribution of species based on 7 species (ethanol, acetaldehyde, methane, carbon monoxide, carbon dioxide, hydrogen and water) as a function of temperature at 1 atm for an equimolar ethanol:water feed. According to their analysis, methane is the dominant species at low temperatures whereas it is hydrogen at high temperatures. As mentioned above, they have also used STA for their analysis. They have predicted the behavior of the system by selecting a particular limited set of reactions (RERs) whose contribution to the system's response is the most significant. As this is the case, here it should be noted that this analysis is limited to equilibrium systems, and hence, the reactions derived only describes the system's response at equilibrium upon changing the operational parameters.

Fishtik et al. [19] finally concluded that at low water concentrations, ethanol decomposes according to:

$$2\,C_2H_5OH \leftrightarrow 3\,CH_4 + CO_2 \quad \text{and,} \tag{8}$$

$$C_2H_5OH \leftrightarrow CH_4 + CO + H_2 \tag{9}$$

Reaction (8) is dominant at lower temperatures, whereas reaction (9) at higher temperatures. The steam reforming reaction, on the other hand, dominates at 700-800 K and with high water:ethanol ratios which also promotes water-gas shift reaction and methane steam reforming:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{10}$$

$$CH_4 + 2\,H_2O \leftrightarrow CO_2 + 4\,H_2 \tag{11}$$

Ioannides [20] has carried out thermodynamic analysis of hydrogen production from ethanol with respect to solid polymer fuel cell (SPFC, also called as PEM fuel cell) applications. The system consisted of a high-temperature steam reforming or partial oxidation (POX) reactor in which ethanol is converted to a gaseous mixture of H_2, CO, CO_2 and CH_4. This reactor is followed by a low-temperature water-gas shift reactor where CO reacts with H_2O giving H_2 and CO_2. As this reaction is equilibrium limited, there is the selective CO oxidation reactor coming afterwards to lower CO below 10 ppm levels. Effluent of the selective CO oxidation reactor is sent to solid polymer fuel cell which is integrated to the system in such a way that when a steam reformer is used, the effluent of SPFC (especially, non-converted hydrogen) is recycled back to reformer to obtain higher conversion efficiencies to electrical energy. As a consequence of this, the system will operate under conditions of incomplete fuel utilization. Ioannides has concluded that, for the steam reforming case, employment of feeds with water:ethanol ratios higher than 3 does not offer any significant advantage as this reduces the overall efficiency as a result of recycling due to increased enthalpy needs for water evaporation in the reformer. Even with lower feed ratios, system with POX reactor gave a slightly better maximum hydrogen yield when compared to the maximum of the system with steam reformer. Systems of POX need higher volumetric flow rates as hydrogen

concentration is lowered due to dilution with nitrogen. However, still they are simpler in construction and exhibit faster response characteristics under transient conditions which is necessary especially for vehicle applications.

Tsiakaras and Demin [21] have studied the thermodynamic analysis of a solid oxide fuel cell system (SOFC) fuelled by ethanol. They fed SOFC with the products of ethanol steam reforming, ethanol reforming with CO_2 and ethanol partial oxidation with air, being in thermodynamic equilibrium. At $T < 950$ K and $T > 1100$ K products of steam reforming gave the maximum efficiency, and at intermediate temperatures, it was reforming with CO_2 leading to maximum. Efficiency obtained by ethanol partial oxidation was, on the other hand, about 20% lower than the maximum.

2.3. Steam Reforming

There are many studies dealing with methanol steam reforming in the literature; however, ethanol steam reforming and hydrogen production from ethanol by autothermal reforming are new areas of study. This section will divide into subsections based on the catalysts used in those studies.

2.3.1. Studies on Supported Cu Catalysts

Choi and Stenger [22] presented the results of experiments of the methanol decomposition reaction catalyzed by a commercial $Cu/ZnO/Al_2O_3$ catalyst both in the absence and presence of water. Tests were performed under catalyst loading of 0.25 – 1.0 g and GHSV of 1000 – 10000 h^{-1}. It was observed that water addition to the feed increased the yield of hydrogen and reduced the formation of by-products like dimethyl ether, methyl formate and methane. However, Choi and Stenger have also concluded that a good methanol synthesis catalyst is not always a good decomposition catalyst especially due to rapid deactivation in the decomposition environment. The causes of this deactivation were listed as copper sintering, carbon decomposition and change of catalyst

structure. For instance, for $Cu/ZnO/Al_2O_3$ catalyst, it has been shown by Cheng [23] that the reduction of ZnO and formation of Cu-Zn alloys cause an initial and rapid decrease of activity for methanol decomposition. In his study, he reported that activity over a Cu/ZnO catalyst is less than that over Cu/Cr/Mn catalyst containing no ZnO.

Choi and Stenger [22] accepted that Cu-O active sites are formed by the dissociative adsorption of water. Therefore, the source of oxygen for the Cu-O site was water in the feed, and copper could be oxidized repeatedly by the following redox mechanism:

$$H_2O + Cu* + 2* \rightarrow 2H* + O - Cu* \quad (12)$$

$$CO + O - Cu* \rightarrow CO_2 + Cu* \quad (13)$$

$$2H* \rightarrow H_2 + 2* \quad (14)$$

A fresh catalyst is largely in the form of oxidized copper after calcination. That is why it should have a higher methanol decomposition rate. If little or no water is fed, the oxidized copper sites reduce to metallic copper which will result in a decrease in activity.

Reddy et al. [24] have reported the synthesis of isobutyraldehyde, which is a very useful chemical feedstock in plastics industry, from methanol and ethanol in a single step over $CuO/ZnO/Al_2O_3$ catalyst. They used ethanol and methanol as the reactants and obtained the following product distribution: Isobutyraldehyde, acetaldehyde, formaldehyde, higher hydrocarbons, acrolein and CO_x. Isobutyraldehyde production increased in the presence of following species: Air < air + H_2O < N_2 < N_2 + H_2O. CuO/Al_2O_3 is a ethanol dehydrogenation catalyst and the basic nature of ZnO promotes this ability. Ethanol is first converted into acetaldehyde which reacts with methanol to produce isobutyraldehyde over $CuO/ZnO/Al_2O_3$.

Catalyst coking and production of by-products like methane, acetaldehyde and diethyl ether, arise as the major problems faced in the studies of ethanol steam reforming. Formation of ethylene during steam reforming leads to catalyst coking [26]. Starting from this, Freni et al. [25] have proposed a two-layer fixed-bed catalytic reactor for ethanol steam reforming reaction. They first converted ethanol into acetaldehyde over Cu/SiO_2 catalyst under low temperature, and then converted acetaldehyde into syngas over Ni/MgO catalyst. They carried out the tests with a total gas flow rate of 218 cm^3/min at GHSV of 109000 h^{-1}, and using a feed of 8.2:1 water to ethanol ratio. Individual runs either with Cu/SiO_2 or with Ni/MgO catalyst only were also performed. The former one resulted in the formation of only acetaldehyde and hydrogen with 100% ethanol conversion up to 500°C. Above this temperature, ethylene formation and catalyst coking, and hence, catalyst deactivation were observed. The latter one, on the other hand, showed a low coking resistance, yet gave high acetaldehyde selectivity. Conversely, the two-layer system produced a species distribution consisting of only hydrogen, carbon dioxide and carbon monoxide (and traces of methane and acetaldehyde) with 100% of ethanol being converted. Match of the exit compositions with the compositions obtained by a simple equilibrium calculation revealed that the following reactions dominate in the overall and reach equilibrium under operating conditions:

$$C_2H_5OH + H_2O \leftrightarrow 2CO + 4H_2 \quad (15)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (16)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (17)$$

Mariño et al. [27] examined the effect of copper loading and calcination temperature on the structure and performance of Cu-Ni-K/γ-Al_2O_3 catalyst. Copper size increases with copper loading and calcination temperature. At low Cu loading and low calcination temperatures low Cu size was obtained which gave high dispersion values. Although also affected by the nature of the active sites, high TOF values were obtained under high dispersions. Thus, they

concluded that ethanol steam reforming reaction is in fact a structure sensitive reaction. Apart from the structure of the catalyst, Cu is an active agent, and Ni promotes C-C bond rupture and increases hydrogen selectivity, and potassium neutralizes the acidic sites of γ alumina which improves the performance of the catalyst.

The above discussion was argued lately again by Mariño et al. [28]. They have re-stated the followings: Metallic copper produces a fast ethanol dehydrogenation to acetaldehyde. Nickel favors the C-C bond rupture of acetaldehyde to produce methane and carbon monoxide. Potassium, on the other hand, prevents dehydration reaction to form ethylene or diethylether by neutralizing the acidic sites of the support.

They further reported that increase in the calcination temperature results in a strong interaction between nickel and aluminum which decreases reducibility of nickel, and along with this, decreases the selectivity towards C_1 compounds. This is in agreement with what had been proposed by Mariño et al. earlier [27].

2.3.2. Studies on Supported Group VIIIB Metal Catalysts

Galvita et al. [29] have used the two-layer fixed-bed catalytic reactor of their previous study (§2.3.1) [25] to test, this time, a palladium-based catalyst and again a nickel-based catalyst in a similar manner. They carried out the experiments by supplying water-ethanol solutions of 8.1:1 and 1.04:1 mol ratios as feed and at WHSV of 1600-2200 cm^3/h-g catalyst. Again, first of all, they tested the catalysts individually. Over Pd catalyst supported on Sibunit[2] only hydrogen, methane, carbon monoxide and carbon dioxide were produced in a range of 210-380°C. It was shown that the following two reactions were taking place:

[2] A special porous carbonaceous material.

$$C_2H_5OH \leftrightarrow CH_4 + CO + H_2 \quad (18)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (19)$$

As water amount in the feed decreased, water-gas shift reaction became less important as it can easily be deduced from Le Châtelier's principle. This shifts the minimum temperature at which 100% ethanol conversion is attainable (330°C) to a slightly higher value (360°C). On the other hand, over the industrial Ni-containing GIAP-16 catalyst, acetaldehyde, methane, hydrogen and carbon oxides were produced. Substantial amounts of coke were also observed.

Alternatively, in the two-layer system, hydrogen, carbon oxides and methane were detected as the products with methane in trace amounts. Temperature of the Pd layer was kept at 335°C, and that of Ni layer was varied between 650 and 800°C. Methane steam reforming reaction took place along with Reaction (18) and Reaction (19) in the overall, all being in equilibrium:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (20)$$

In a later study of Galvita et al. [30] characteristics of the Pd catalyst and its catalytic performance in ethanol decomposition in steam were discussed in more detail. TEM micrographs and XP spectra of both fresh and sent catalysts showed no difference. In order to identify the intermediate species, the mechanism of the overall reaction taking place, and the fast and slow steps in the reaction pathway, WHSV was increased from 2200 to 33000 cm^3/h-g catalyst. At the end the following mechanism was proposed:

$$C_2H_5OH \leftrightarrow CH_3CHO + H_2 \quad (slowest) \quad (21)$$

$$CH_3CHO \rightarrow CH_4 + CO \quad (fast) \quad (22)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (slow) \quad (23)$$

Freni [31] has tested Rh/Al_2O_3 catalyst and the alumina support for ethanol steam reforming reaction for molten carbonate fuel cell applications. He showed that alumina results in dehydration of ethanol forming ethylene and water at temperatures higher than 600 K for a feed consisting 90% water. He further showed that water content of the feed does not influence the ethylene formation. Rh/Al_2O_3 catalyst, on the other hand, produced carbon monoxide and methane below 730 K (with ethanol dehydrogenation into ethoxide as the intermediate step), and above this temperature ethanol steam reforming prevailed with 100% ethanol conversion and no yield of C_2H_4 or CH_3CHO. The time-on-stream data showed no selectivity changes; however, ethanol conversion decreased with time. This is attributed to the loss of the catalyst dispersion degree as a result of a size modification of the catalyst particles under thermal effect of the reaction temperature which caused catalyst grains to grow.

Fatsikostas et al. [32] presented the results of the experiments done on Ni/La_2O_3, and reported that this catalyst shows high activity, high hydrogen selectivity, as well as good long term stability. They conducted the tests in a temperature range of 300-800°C sending a feed of 3:1 water-ethanol ratio at a space time (W/F) range of 0.01 to 0.23 g catalyst.s/cm^3. Tests carried out at very high space time (0.0375 g catalyst.s/cm^3) showed that ethanol steam reforming takes place to a significant extent above 400°C. 100% ethanol conversion was achieved only at about 700°C. Furthermore, it is the ethanol dehydrogenation that is the dominant reaction at low temperatures which becomes less important above 500°C as acetaldehyde begins to reform. As La_2O_3 does not have an acidic nature no ethylene is produced. At high temperatures the only reaction products were carbon monoxide and hydrogen, with carbon dioxide (from water-gas shift reaction) and methane (from methanation reaction[3]) as being the by-products. Tests on different space velocities also revealed that at contact times higher than 0.1 g catalyst.s/cm^3 (at 750°C) it is possible to achieve 100% ethanol conversion and hydrogen selectivities higher than 95%. Time-on-stream data, on the other

[3] $2CO + 2H_2 \leftrightarrow CH_4 + CO_2$

hand, proved the stability of the catalyst only with a little deactivation as a result of decrease in ethanol conversion, although no significant change in hydrogen selectivity was observed.

Table 2. *Effects of process parameters in the study of Liguras et al. [33]*

Parameters	**Effect on/of**	**Observation**
Metallic Phase 1% *Me*/γ-Al_2O_3	X_{C2H5OH}	Rh >> Pt > Pd > Ru
	S_{H2}, S_{CO}	Rh >> Pt > Ru = Pd
	S_{CO2}	All but especially Pt, Rh
	S_{CH3CHO}, S_{C2H4}	All but especially Rh
	S_{CH4}	None. Rh, a little
Metal Loading *0.5-2%* Rh/γ-Al_2O_3 *1-5%* Ru/γ-Al_2O_3	Increase in Rh amount	$T_{100\%\ conv}$, S_{H2}, $S_{CO2}\uparrow$ $S_{CO} \rightarrow$ $S_{byprod} \downarrow$
	Increase in Ru amount	S_{H2}, S_{CO2}, $S_{CO}\uparrow$ $T_{100\%\ conv}$, $S_{byprod} \downarrow$
5% Ru/*Support*	X_{C2H5OH}, S_{prod}, S_{byprod}	Al_2O_3 > MgO > TiO_2
Space velocity (W/F) *0.018-0.105 g catalyst.s/cm^3*	Increase in W/F	X_{C2H5OH}, S_{H2}, $S_{CO}\uparrow$ S_{CO2}, $S_{byprod}\downarrow$

Liguras et al. [33] have investigated the effect of Rh, Ru, Pt and Pd catalysts supported on Al_2O_3, MgO and TiO_2 and the effect of metal loading on the catalytic performance towards ethanol steam reforming. They performed the experiments feeding ethanol and water in stoichiometric ratios with respect to ethanol steam reforming reaction giving CO_2. They worked under W/F range of

0.018 to 0.105 g catalyst.s/cm^3, and at a temperature range of 600-850°C. Complete conversion was obtained at 800°C under severe conditions over 1% Rh/Al_2O_3 catalyst. Acetaldehyde, ethylene (over acidic alumina) and methane (from hydrogenation of carbon oxides) were formed as by-products, yet with low selectivities. At temperatures near 800°C, selectivity of ethylene decreased to zero (as that of acetaldehyde) due to steam reforming of ethylene. Effects of all process parameters are summarized in Table 2 for this study. Finally, long-term stability test was also carried out for 5% Ru/Al_2O_3 catalyst and the results were similar to what has been reported by previous studies [31,32]: No change in hydrogen selectivity (and selectivity to methane, acetaldehyde and ethylene), decrease in ethanol conversion.

Cavallaro et al. [34] also studied the ethanol steam reforming on Rh/Al_2O_3 catalyst, and investigated the influence of reaction temperature (550-650°C), water:ethanol ratio (4.4-12.4), space velocity (5000-30000 h^{-1}) and oxygen in the reacting medium. Results of the experiments showed that high temperatures and low space velocities are necessary to optimize hydrogen production. Runs performed at different GHSV values revealed that ethanol first dehydrogenates into acetaldehyde which either decomposes into methane or reforms with steam into hydrogen. Methane further undergoes steam reforming. Steam reforming of methane occurs with a lower rate respect to water-gas shift reaction. On the other hand, acetaldehyde decomposition is faster compared to ethanol dehydrogenation. Furthermore, catalyst deactivation caused by metal sintering and coke formation was registered. Addition of oxygen, alternatively, promoted not only metal sintering as a result of hot spot phenomena but also the ethanol conversion through oxidative dehydrogenation:

$$C_2H_5OH + \tfrac{1}{2}O_2 \leftrightarrow CH_3CHO + H_2O \qquad (24)$$

Deluga et al. [7] have also studied hydrogen production from ethanol and ethanol-water mixtures over rhodium catalyst, however, supported on ceria.

Alternatively they have studied autothermal reforming, and obtained 100% hydrogen selectivity with more than 95% ethanol conversion under as high a space velocity as 360000 h^{-1}, and even under higher velocities than this one. They carried out the runs at 140°C. Yet the catalyst temperature reached about 700°C as oxidation reaction was also taking place. They have also performed a simple economic analysis considering an ethanol cycle starting from photosynthesis and ending in a perfect fuel cell. They concluded that under such a hypothetic, completely reversible, ideal system the fuel cost (cost of ethanol to generate electricity) would be about $0.04 per kWh. They finally suggested that it may be possible to capture more than 50% of the energy from photosynthesis as electricity.

Llorca et al. [35] have studied the effect of supports of cobalt catalysts on ethanol steam reforming under a mixture of 1:13:70 ethanol:water:argon (molar ratio) in a temperature range of 300-450°C and at 5000 h^{-1} GHSV. Supports tested are the following: MgO, γ-Al_2O_3, SiO_2, TiO_2, V_2O_5, ZnO, La_2O_3, CeO_2 and Sm_2O_3. Ethanol steam reforming occurred to a large extent over ZnO-, La_2O_3-, Sm_2O_3-, and CeO_2-supported catalysts. Different GHSV values and/or different Ar to ethanol and water ratios were also studied over Co/ZnO catalyst which showed the best result in terms of 74% hydrogen selectivity under 100% ethanol conversion. These experiments revealed that as GHSV increases decomposition of ethanol to acetone decreases while the extent of the steam reforming reaction increases. Further increase of GHSV increased the selectivity to acetaldehyde which proved ethanol dehydration to be an intermediate step in ethanol steam reforming.

2.3.3. Comparative Studies

This subsection includes studies comparing Group VIIIB metal catalysts both among each other and with other catalysts, and different oxide catalysts.

Cavallaro and Freni [36] tested several catalysts for ethanol steam reforming to be used indirectly in molten carbonate fuel cells (MCFCs). As the operating temperature of MCFC is above 900 K, the results of the experiments carried out at atmospheric pressure were extrapolated to temperatures 800-900 K and pressures up to 100 bar by using a mathematical model. Experiments done at high temperatures (630-750 K) showed no trace of intermediate oxidation products like acetaldehyde, acetic acid or ethyl acetate the production of which are more important on copper catalysts. For temperatures lower than 600 K, however, the selectivity to carbon dioxide and hydrogen decreases due to higher oxygenate formation. It was observed that acetic acid selectivity is directly related to the water:ethanol ratio, whereas ethyl acetate selectivity seems to be related to conversion and temperature. Runs with different space velocities revealed that acetaldehyde is produced as the first step which is followed by an oxidative step to ester (under slightly excess water) or to acetic acid (under excess water). All catalysts tested shifted the system towards equilibrium above 630 K. $CuO/ZnO/Al_2O_3$ and $NiO/CuO/SiO_2$ catalysts do not produce coke and/or oxygenated side-products even with water:ethanol ratio lower than 3 although some catalysts require ratios higher than 4. Noble metal (Pt, Rh) and W-based catalysts showed almost the same activity as $CuO/ZnO/Al_2O_3$. Finally, mathematical model showed that it is possible to obtain good hydrogen yields of 30-50% even at high pressures (which thermodynamically reduce hydrogen selectivity) in MCFC separated from the reformer side by a membrane.

Takezawa and Iwasa [37] argue that the differences in catalytic performances of copper and Group VIIIB metals in methanol steam reforming and methanol dehydrogenation are due to the differences in the reactivity of HCHO intermediate involved. In the beginning of their study, they summarize all information available in the previous studies on copper and Group VIIIB metal catalysts. Firstly, over copper and Pd/ZnO catalysts, methanol dehydrogenates into acetic acid; whereas over other Group VIIIB metals syngas is formed from methanol as shown below, respectively:

Table 3. *Mechanisms and products in the study of Takezawa and Iwasa [37]*

Feed	Catalyst	Reaction Mechanisms and/or Product Distributions
CH_3CHO/ H_2O	VIIIB metal/SiO_2	Methanol decomposition (main) $CH_3OH \rightarrow CO + 2H_2$ Steam Reforming $CH_3OH \rightarrow CO + 2H_2 \xrightarrow{H_2O} CO_2 + H_2$
	Cu, Cu/SiO_2	Steam Reforming $CH_3OH \xrightarrow{-H_2} HCHO \xrightarrow{H_2O\,(or\ HO-)} HCOOH\,(or\ HCOO-) \rightarrow CO_2 + H_2$
$HCHO$/ CH_3OH	Cu, Cu/SiO_2	Acetic acid formation $CH_3OH \rightarrow HCHO \xrightarrow{CH_3OH\,(or\ CH_3OH-)} HCOOCH_3$
	Pt/SiO_2, Pd/SiO_2	Formaldehyde decomposition (main) $HCHO \rightarrow CO + H_2$ Methanol decomposition $CH_3OH \rightarrow CO + 2H_2$
C_2H_5OH/ H_2O	Cu/SiO_2	Products: CH_3COOH (main), CH_3CHO, H_2, C_4-species
CH_3CHO/ H_2O	Cu/SiO_2	Products: CH_3COOH, H_2 (Also: Butyraldehyde, ethanol) Steam reforming of acetaldehyde (main) $CH_3CHO + H_2O \rightarrow CH_3COOH + H_2$ Hydrogenation of acetaldehyde $CH_3CHO + H_2 \rightarrow C_2H_5OH$
C_2H_5OH	Pd, Pt, Ni	Products: CH_4, CO, H_2, CH_3CHO Dehydrogenation of ethanol $C_2H_5OH \rightarrow CH_3CHO + H_2$ Decomposition of acetaldehyde $CH_3CHO \rightarrow CH_4 + CO$

- $2CH_3OH \leftrightarrow HCOOCH_3 + 2H_2$ (25)
- $CH_3OH \leftrightarrow CO + 2H_2$ (26)

On the other hand, copper and Pd/ZnO catalysts hydrogenate unsaturated aldehydes/ketones to unsaturated alcohols while other Group VIIIB metal catalysts to saturated aldehydes/ketones. Also, hydrogenation of esters and carboxylic acids to alcohols which is dominant over Pd/ZnO catalyst occurs more over Cu catalysts when compared to other Group VIIIB metal catalysts.

In this study, Takezawa and Iwasa further tested Cu, Ni, Rh, Pd and Pt catalysts supported on various oxides (MgO, La_2O_3, Nd_2O_3, MnO_2, Cr_2O_3, HfO_2, Na_2O_5, Al_2O_3, SiO_2, ZnO) feeding different mixtures to the reactor to understand the reaction mechanisms taking place. Reactions taken place and product distributions obtained are summarized in Table 3 for various mixtures fed to the system.

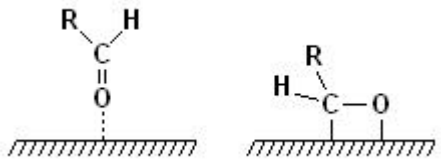

Figure 5. *Adsorption of aldehydes on IB (left) and VIIIB metals [37]*

It was re-stated in the study that adsorption of aldehydes on IB and VIIIB metals occur differently as shown in Figure 5 which is the basic reason of the difference in the reactivity of formaldehyde intermediate, HCHO, and hence, the product distributions obtained as indicated in Table 3.

As mentioned above, catalytic activity of Pd/ZnO catalyst is similar to that of copper catalysts. This is because formaldehyde adsorbs on positively charged Pd sites of the PdZn alloy formed. On the other hand, the highest selectivity for steam reforming was obtained over Pd catalysts which increased with increase in temperature. Best performance was obtained at 30wt% Pd loading.

In a later study, Iwasa et al. [38] have produced acetaldehyde at low conversion levels and at high space times over Pd-Zn, Pd-Ga and Pd-In alloys of Pd catalysts as also produced over Cu/ZnO catalyst. At higher temperatures and lower space times, formation of ethyl acetate was observed with some decrease in acetaldehyde selectivity suggesting that ethyl acetate was produced through acetaldehyde. Over metallic Pd, however, decomposition of ethanol to CO and CH_4 took place. Iwasa et al. have also pointed out the effects of different catalyst preparation methods on activity tests of the same catalyst.

Aupretre et al. [4] investigated the nature of metals and oxides to maximize hydrogen production while minimizing carbon monoxide formation. They used a feed of (12.8 vol% ethanol + 38.4% water + 48.8% N_2) to reach a total flow rate of 100 cm^3/min. They carried out the experiments at 500-800°C. They proposed a mechanism such that ethanol is to be activated on the metal and water on the support. Based on this mechanism, Rh, Pt, Pd, Ru, Ni, Cu, Zn and Fe were tested along with Al_2O_3, CeO_2-Al_2O_3, CeO_2, CeO_2-ZrO_2 and ZrO_2 as the oxide supports. Results of the experiments showed that carbon dioxide is produced in ethanol steam reforming; therefore, metals to be used in active and selective catalysts for ethanol steam reforming should be highly active in steam reforming, and poorly efficient in water-gas shift reaction. To improve performances of the catalyst in steam reforming ceria-containing supports were used which enable enhanced OH surface mobility, and promote water-gas shift reaction. Rh and Ni catalysts are active for steam reforming and not for water-gas shift reaction. Table 4 summarizes the results obtained over those catalysts. As a final note, Pt, Cu, Zn and Fe catalysts supported on γ-Al_2O_3 was highly

Table 4. *Effect of supports on H_2 yield and CO_2 selectivity in the study of Aupretre et al. [4]*

Parameter	Effect on	Observation
1% Rh/*Support*	H_2 yield	$Ce_{0.63}Zr_{0.37}O_2$ > 12%CeO_2-γ-Al_2O_3 > CeO_2 > γ-Al_2O_3
	CO_2 Selectivity	γ-Al_2O_3 > 12%CeO_2-γ-Al_2O_3 > CeO_2 > $Ce_{0.63}Zr_{0.37}O_2$
9.7% Ni/*Support*	H_2 yield	$Ce_{0.63}Zr_{0.37}O_2$ > CeO_2 > 12%CeO_2-γ-Al_2O_3 > γ-Al_2O_3
	CO_2 Selectivity	γ-Al_2O_3 > 12%CeO_2-γ-Al_2O_3 > CeO_2 > $Ce_{0.63}Zr_{0.37}O_2$

Table 5. *Summary of the results of the study by Llorca et al. [39]*

Oxide	Nature of active site	Observation
SiO_2	-	No conversion
MgO	Basic	High acetaldehyde selectivity, negligible steam reforming
γ-Al_2O_3	Acidic	Ethylene as the only product
V_2O_5	Acidic	Ethylene as the major product
La_2O_3	Basic	Ethylene as the major product
Sm_2O_3	Basic	Ethylene as the major product
ZnO	Basic, redox property	Ethanol decomposes to acetone and acetaldehyde over basic sites. Redox characteristics help acetaldehyde to convert into hydrogen.

active for water-gas shift reaction although they showed moderate activity for steam reforming.

Llorca et al. [39] tested various oxides for steam reforming reaction at 300-450°C. Results of this study are listed in Table 5. Best performance was obtained by ZnO which gave highly effective production of CO-free hydrogen with 100% ethanol conversion.

CHAPTER 3

EXPERIMENTAL AND METHODOLOGY

In this study, ZnO/SiO_2 catalysts with different copper and palladium loadings, and Co doped SBA-15 catalyst were prepared by different sol-gel techniques, characterized to some extent by Thermal Gravimetric Analysis (TGA), and Brunauer-Emmett-Teller (BET) techniques, and tested for their activity and selectivity in ethanol steam reforming in a packed-bed reactor.

3.1. Catalysts Tested

Catalysts used in this study are listed in Table 6 along with their compositions in weight percents. Set I catalysts comprise promoted and/or supported zinc oxide catalysts, and Set II catalyst is the SBA-15-supported cobalt catalyst. Samples 4,

Table 6. *Compositions of the catalysts tested*

	Sample No.	**Compositions**
Set I	1	6%Cu/50%ZnO/SiO_2
	2	4%Cu/50%ZnO/SiO_2
	3	2%Pd/50%ZnO/SiO_2
	4	50%ZnO/SiO_2
	5	50%ZnO/SiO_2
	6	50%ZnO/SiO_2
Set II	7	40%Co/SBA-15

5 and 6 differ from each other by different water amounts used during preparation.

Set I catalysts were prepared at Izmir Institute of Technology and Set II catalyst was prepared in the Department of Chemistry at METU. Further information on the preparation and characterization of these catalysts is given in Appendices B and C.

3.2. Experimental Setup and Activity Measurements

Systems of liquids and gases can become much more complicated, and hence, challenging than it can ever be imagined. A huge portion of this study was spent on establishing a proper experimental setup and especially on finding an answer to how to feed the liquid to the system. After many systems designed, many unsuccessful experiments performed, and many modifications made the setup shown in Figure 6 was put into operation. Below is an explanation on the experimental setup and how activity measurements are carried out.

Ethanol and water mixtures are prepared in ratios according to the stoichiometry of the steam reforming of ethanol to carbon dioxide and hydrogen: 25 mol% (46 wt%) ethanol. The liquid mixture is then injected into a cooler of 25 cm^3 kept at 3°C to minimize vaporization effects as the level decreases in the cooler during experiments. A peristaltic pump is used to feed this liquid to the system shown in Figure 6 at an average flow rate of 0.047 cm^3/min. The liquid is firstly sent to a bulb of 250 cm^3 kept at 160°C by means of heating tapes. Collected in the bulb the vaporized liquids are then directed to the inlet of the reactor and carried into the reactor under a nitrogen and argon flow of 45 cm^3/min and ca. 4 cm^3/min, respectively, as shown in the enlarged view in Figure 6.

A packed-bed reactor having an inner diameter of 3.8 mm is used for reactivity tests. 0.1 g catalyst is used in each experiment, and the catalyst bed is supported

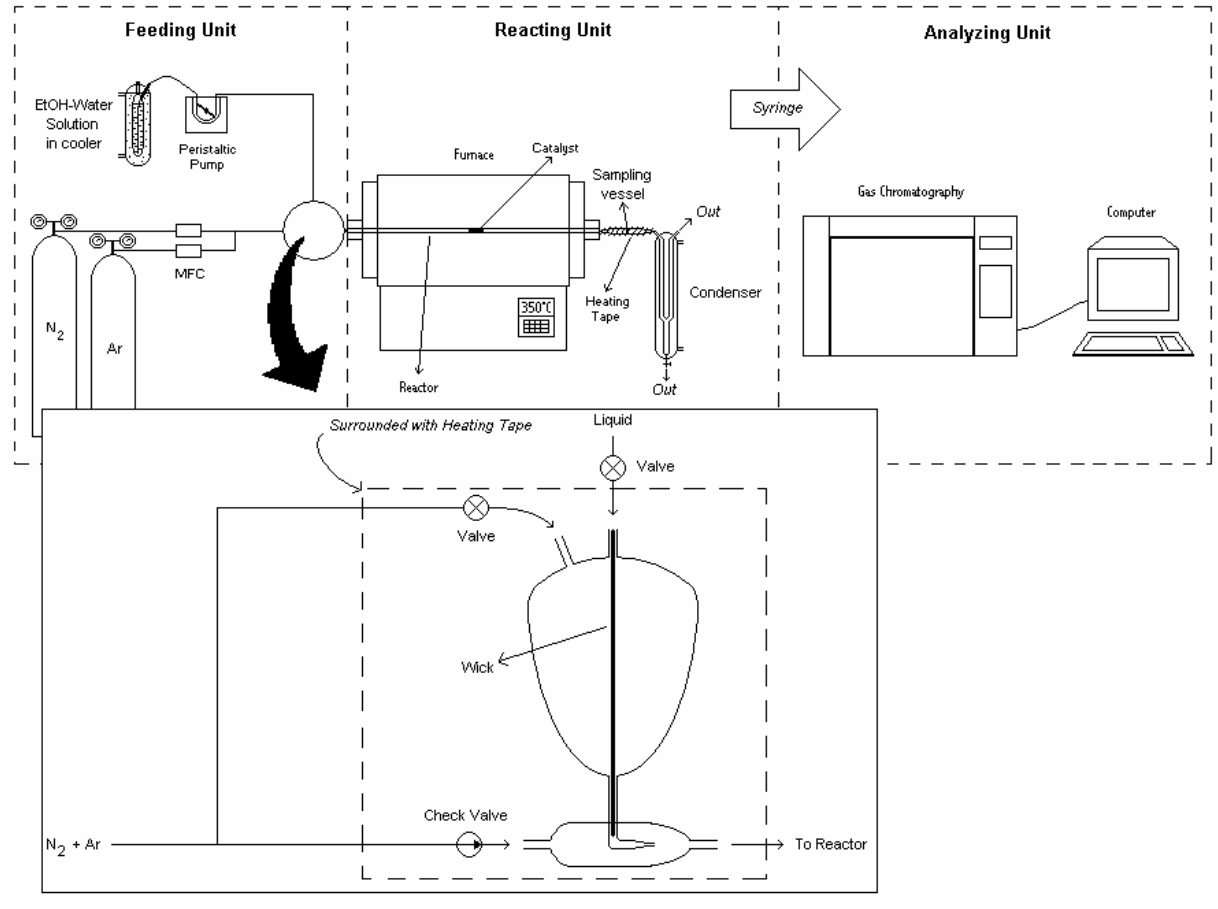

Figure 6. *Experimental Setup*

by quartz wool at both ends. A tubular furnace is used to keep the temperature of the reactor constant at desired values.

Product stream exiting the reactor then flow into a "sampling vessel" which is also heated by heating tapes and kept at 175°C. Sampling vessel has an opening, other than its two ends, which is closed by a septum. Samples are taken into heated gas syringes through this septum to be analyzed. Species which are in liquid phase under room temperature were condensed next in a condenser kept at 3°C. Gaseous species are discharged into atmosphere through fume hoods while liquefied species are collected in bottles for proper disposal.

Analyses were carried out in a gas chromatograph (GC) (HP 4890A) equipped with a Thermal Conductivity Detector (TCD) which uses nitrogen as reference gas. Species are separated in a GasChrom MP-1 packed column (30 ft). Table 7 lists the values of GC settings used during analyses. A long column, low flow rates and a temperature ramp in the oven are necessary for such a system containing components like hydrogen which rapidly adsorbs and desorbs in every column, and components like ethanol which is just the opposite. For this reason, analysis of one sample takes about 1 hour.

Table 7. *GC settings*

GC Settings	**Values**
Injection port temperature	220°C
Oven temperature	75°C (9 min) [4°C/min] 200°C (9.5 min)
Detector temperature	250°C
Reference flow	9-10 cm^3/min
Column flow	13-15.5 cm^3/min

Single-point GC calibration was carried out for each species in most of the experiments. For the others, previous calibration data were processed to obtain a collective representative calibration data as explained in detail in Appendix E.

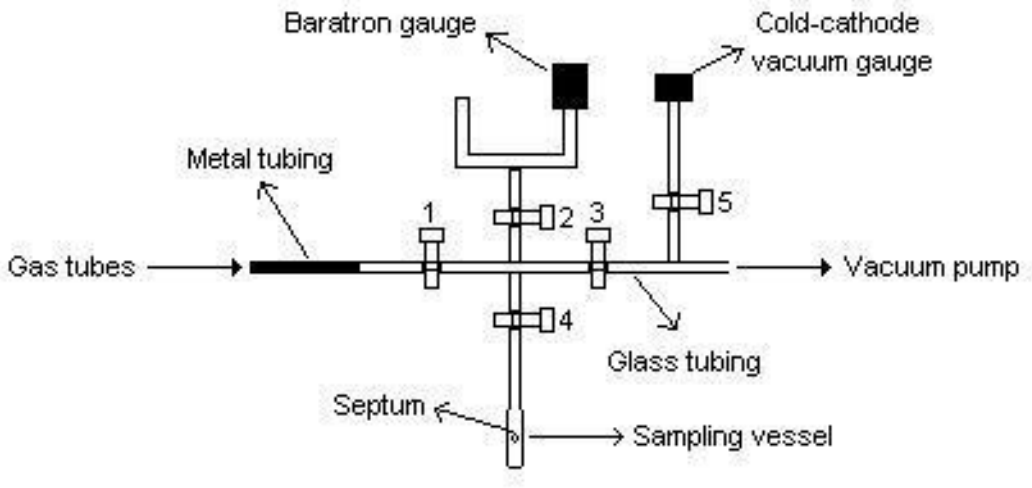

Figure 7. *Manifold used for GC calibration*

Figure 7 shows the manifold used for GC gas calibration. Manifold is firstly vacuumed by a vacuum pump. After closing valve 3, a single gas or a calibration gas[4] with known compositions is sent to the system. The gas is then collected at room temperature and atmospheric pressure in the space obtained by closing valves 1 and 3. The pressure of this gas, and hence, its amount are controlled by a read-out connected to the Baratron gauge. A certain volume is taken into a gas syringe and injected to GC to obtain a mol-to-area relation. On the other hand, liquid calibration is done by using microliter liquid syringes, and a known volume of sample is again injected to GC to get the mol-to-area relation.

[4] Containing carbon monoxide, methane, carbon dioxide and ethylene.

Experiments are carried out at temperatures between 300 and 500°C at intervals of 50°C. Before each experiment the system is heated up under the flow of nitrogen and argon. As the system reaches thermal equilibrium, liquid starts to be fed at which point the valve in the liquid line is opened and the valve in the gas line is closed (Figure 6). Previous experiments showed that no reaction takes place below 300°C. As this is the case, one additional set is performed also at either 200 or 250°C to obtain ethanol and water amounts sent to the system in gaseous phase. Although these values could as well be obtained from liquid pumping flow rate (as already done), as will be discussed in the following chapter, most of the time those values do not come out to be *near*. Some experiments were carried out starting from 200 or 250°C, and by increasing the reactor temperature to 300°C, and then to 350°C and so on. As heating of the furnace is rather rapid compared to its cooling additional time is allowed for the system to re-establish steady state at each temperature. Some experiments, on the other hand, were done starting at 500°C and by letting the furnace cool down which is already a time-consuming process, and the system remains in steady state at each cooling step so no additional time is waited. A sample time schedule of one full experiment is given in Appendix F. At each set, or reactor temperature; one, two or three samples are taken and analyzed in GC sequentially. Before each injection, syringe is heated by a heating gun, and after each injection, syringe is cleaned by a syringe cleaning equipment as shown in Figure 8. Other pictures of the setup are given in Appendix G.

As the total flow rate of the "heated" gaseous mixture at the reactor exit is to be known to do the necessary calculations, which cannot easily be measured by means like soap bubble flow meter, the flow rate is calculated indirectly from a known constant flow rate of a known inert gas component also sent to the system. Nitrogen, the carrier, could have been used for such a purpose; however, it would be impossible to obtain a nitrogen peak in the chromatogram as the reference gas to the GC is already nitrogen. So, argon was used and sent with nitrogen to the system as mentioned above. Use of argon alone both as the

carrier and the *internal standard* would also be of no use as the GC column would saturate with argon which would result in a faulty argon area.

Figure 8. *Heating gun (left) and syringe cleaning equipment*

Few experiments were conducted also under air flow to realize some ethanol oxidation along with ethanol steam reforming, or in other words autothermal reaction. Argon could not be used in these experiments as oxygen in air could not be separated from argon in the column. So, no calibration was done in these experiments as the total flow rate was not known, and instead, the collective calibration data were used to carry out the calculations. Table 8 summarizes the

Table 8. *Flow rates and compositions of liquid and gaseous phases*

	Unit	[5]	Total	Ethanol	Water	Nitrogen	Oxygen
Liquid phase	cm^3/min		0.047	0.012	0.035	-	-
	g/min		0.043	0.020	0.023	-	-
	mol/min		0.0017	0.00044	0.0013	-	-
	mol% or vol%		100	25	75	-	-
	wt%		100	46	54	-	-
Gaseous phase	cm^3/min	S	86	10	31	45	0
		H	86	10	31	36	9.4
		L	51	10	31	0	9.4
	g/min	S	0.096	0.020	0.023	0.053	0
		H	0.091	0.020	0.023	0.042	0.0064
		L	0.049	0.020	0.023	0	0.0064
	mol/min	S	0.0036	0.00044	0.0013	0.0019	0
		H	0.0037	0.00044	0.00131	0.0015	0.00040
		L	0.0021	0.00044	0.0013	0	0.00040
	mol% or vol%	S	100	12	36	52	0
		H	100	12	36	41	11
		L	100	20	61	0	19
	wt%	S	100	21	24	55	0
		H	100	22	25	46	7.0
		L	100	40	47	0	13

[5] Steam reforming: S. Autothermal reforming: H (High space velocity), L (Low space velocity)

compositions and flow rates of both the liquid phase and the gaseous phase applied in experiments.

Parameters changed in experiments include catalysts, temperature and space velocity. Following chapter presents the results of these tests along with comments and discussions.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Characterization Results

BET results of both Set I and Set II catalysts (except Sample 5) are shown in Table 9. For Set I catalysts, as seen in the table, as the amount of metal used in the catalyst increases, BET surface area decreases while average pore diameter also increases.

Cannas et al. [40] have also come up with a similar situation. They observed crystallite phases in XRD patterns and a decrease in BET surface areas as they impregnated more ZnO on silica. They attributed this to the involvement of larger areas of support as the dispersing phase (ZnO) is in higher amount. This way, the dispersing phase is spread over the surface in a homogeneous way. Increase in the amount of metal used in the catalysts may have resulted in formation of larger and denser silica suspensions which end up with having such BET areas as explained by Cannas et al. [40].

Cannas et al. also presented the results of XRD patterns of their ZnO/SiO_2 catalysts as the calcination temperature increases. According to their data, ZnO zincite phases were observed in catalysts calcined at temperatures between 500 and 700°C. So, it is very likely to have zincite phases in our catalysts. Above 800°C, however, a solid state reaction between zinc oxide and the silica matrix was detected by Cannas et al. which resulted in the formation of zinc silicates like β-Zn_2SiO_4. Such zinc silicate formations might have also occurred as a result of a probable catalytic effect of palladium and/or copper to lower the

necessary reaction temperature from 800°C to our calcination temperature, 500°C.

Table 9. *BET results*

Catalyst			BET Surface Area (m^2/g)	BJH Desorption Average Pore Diameter (nm)
Set I	1	6%Cu/50%ZnO/SiO_2	94	7.7
	2	4%Cu/50%ZnO/SiO_2	144	7.6
	3	2%Pd/50%ZnO/SiO_2	77	6.6
	4	50%ZnO/SiO_2	170	3.3
	6	50%ZnO/SiO_2	181	3.7
Set II	7	40%Co/SBA-15	747	3.5

4.2. Reactivity Test Results

Results of ethanol steam reforming tests both in the absence and presence of oxygen or air over all catalysts except sample 5 are given below.

4.2.1. Ethanol Steam Reforming

Steam reforming tests were carried out over Set I catalysts. Table 8 summarizes flow rates and compositions of both liquid and gaseous mixtures sent to the system. This way, for all experiments space velocities were kept around 54000 cm^3/h-g catalyst using 0.1 g of catalyst (corresponding to 81000 h^{-1}, or space

time of 0.07 g catalyst.s/cm^3, 0.045 s) which is well above the values used in literature as indicated in Chapter 2.

As will be presented soon the results showed that promoted and non-promoted ZnO/SiO_2 catalysts used act as ethanol dehydrogenation catalysts over the temperature range of 300-500°C. Although traces of ethylene (also at 450°C), methane and carbon dioxide were observed at the reaction temperature of 500°C, each of them accounted for less than 1% of the total products including

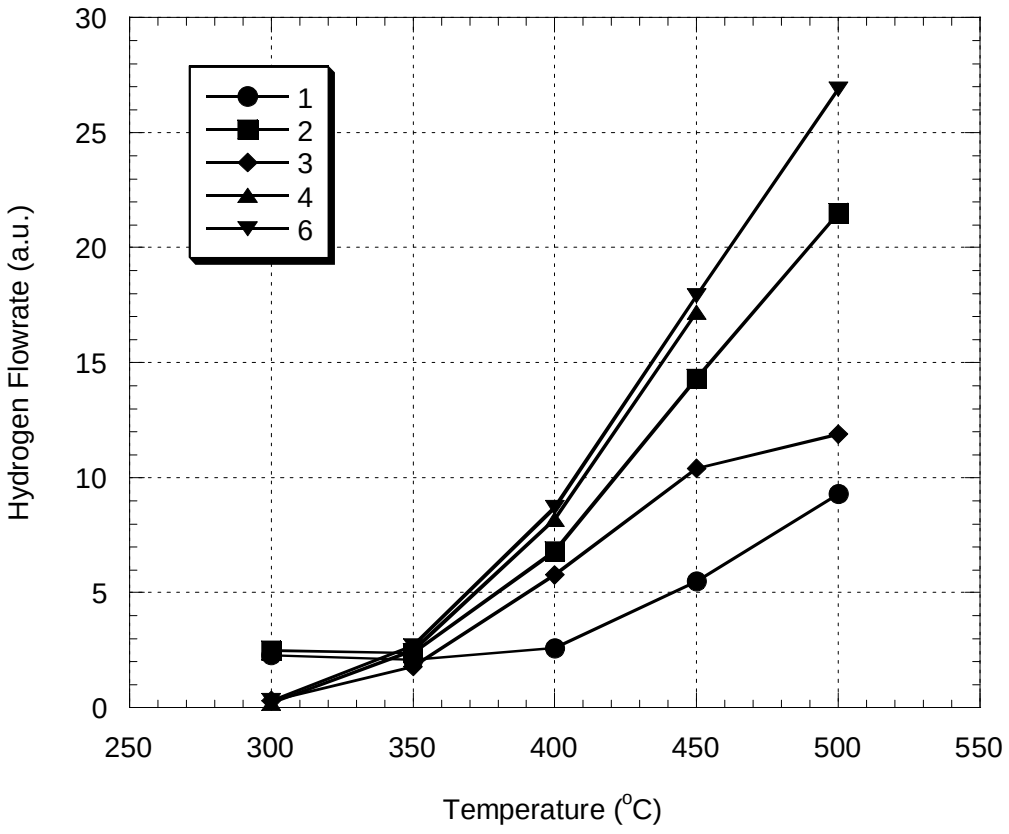

Figure 9. *Effect of temperature and catalyst on hydrogen flow rate (Calculated parameters: EtOH:H_2O=1:3, GHSV~54000 cm^3/h-g catalyst, flow rate~86 cm^3/min. Measured parameters: Mass of catalyst=0.1 g.)*[6]

[6] Calculated parameters include gas phase parameters obtained from ideal gas law.

unconverted reactants obtained at the exit of the reactor. On the other hand, no carbon monoxide was produced. From fuel cell application's point of view, carbon monoxide-free hydrogen is something desired, yet acetaldehyde has also poisoning effect on electrodes of fuel cells as carbon monoxide do.

Figures 9 and 10 present the results obtained as hydrogen and acetaldehyde flow rates, respectively, given in arbitrary units.

As only acetaldehyde and hydrogen were produced over Set I catalysts, Figures 9 and 10 can also be regarded as selectivity plots towards hydrogen and

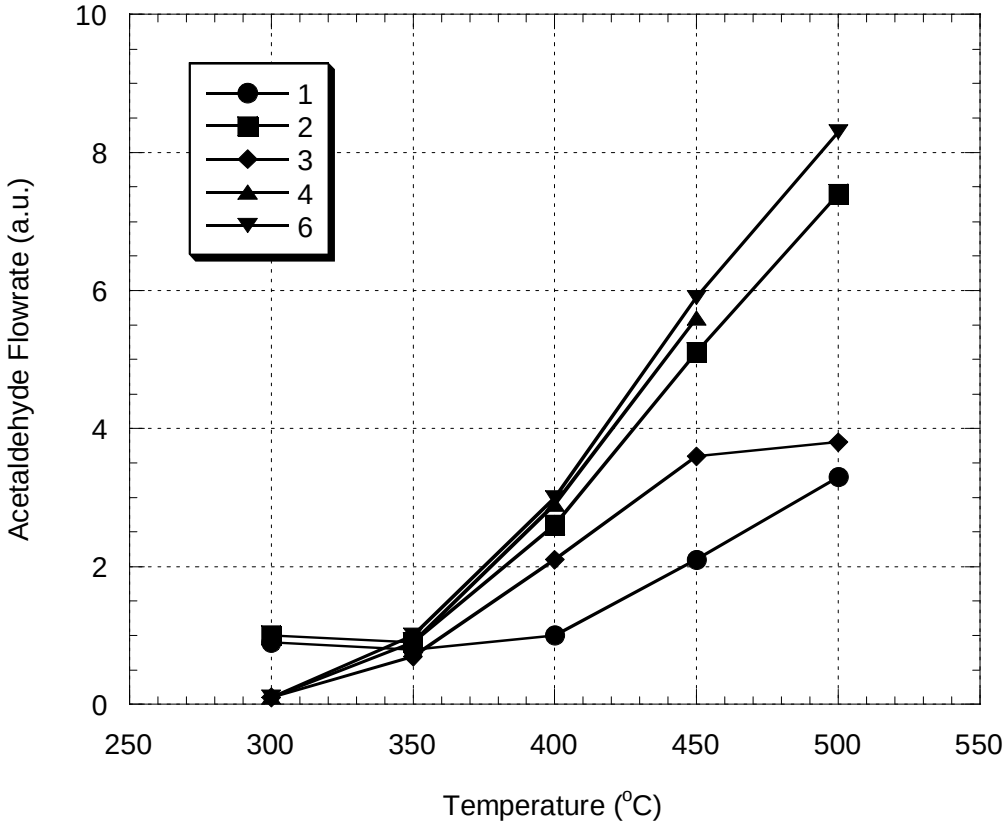

Figure 10. *Effect of temperature and catalyst on acetaldehyde flow rate (Calculated parameters: EtOH:H_2O=1:3, GHSV~54000 cm^3/h-g catalyst, flow rate~90 cm^3/min. Measured parameters: Mass of catalyst=0.1 g.)*

acetaldehyde, respectively, and even as ethanol conversion plots, each of which having appropriate units of scale. Although not explicitly calculated and plotted, hydrogen selectivity can be defined as the ratio of the produced moles of hydrogen to the moles of hydrogen equivalent to the consumed moles of ethanol.

As seen in Figure 9, below 350°C copper-promoted catalysts (1 and 2) showed better selectivity to hydrogen. At 400°C and above this temperature, on the other hand, non-promoted catalysts appear to be superior to other catalysts in ethanol dehydrogenation. In this temperature range, 4%Cu-promoted catalyst (2) showed better results compared to Pd-promoted catalyst (3). 6%Cu-promoted catalyst (1), however, came into view with the poorest performance.

Trends in acetaldehyde flow rate, as seen in Figure 10, are very similar to those observed for hydrogen in Figure 9. This was in fact an expected result as nothing other than ethanol dehydrogenation is taking place over the catalysts: Multiplication of each and every point having arbitrary unit in Figure 10 by an average factor of 2.8 gives the data of Figure 9. This calculation also shows the consistency of the analyses carried out by GC since both hydrogen and acetaldehyde flow rates should be equal as they were produced equimolar by the only reaction, ethanol dehydrogenation.

ZnO/SiO_2 mixed oxide shows both acidic (Lewis acid) and basic properties [41]. Ethanol dehydrogenation occurs over basic sites of the catalyst which are capable of dissociating H-H and C-H bonds of ethanol [24,39,42]. Ethanol dehydration to ethylene, on the other hand, takes place over acidic sites [11,28,32,33,39,42]. As none of the catalysts has produced some remarkable amount of ethylene, it can be said that all Set I catalysts act as bases under reaction conditions. However, basicity of the catalysts decreases upon metal promotion.

Cu catalysts, especially Cu/ZnO, are known as active catalysts for acetaldehyde hydrogenation [12,13,16]. It has also been shown that over metallic copper, and

alumina-, silica- and zinc oxide-supported copper catalysts acetaldehyde and hydrogen can be produced with almost 100% ethanol conversion [24,25,27,28,38]. On the other hand, it has also been demonstrated that over some Pd catalysts again acetaldehyde and hydrogen were obtained as the only products [29]. Pd-Zn alloys formed during the preparation of Pd/ZnO catalysts help them exhibit similar catalytic activities with copper catalysts [37]. Acetaldehyde was also produced over Pd-Zn alloys of Pd/ZnO catalysts [38].

As such studies are available in literature it was no surprise to obtain such a product distribution over Set I catalysts. Yet, it is interesting to get poorer results with metal promoted ones. From above discussion, it can be deduced that dehydrogenation of ethanol took place over Pd/Zn alloys in sample 3. And, poor activities compared to non-promoted catalysts can be attributed to the presence of zinc silicates and metal zincates (like Pd/Zn) in pores, closed at the ends, which are, therefore, not accessible to reacting molecules. This may also explain the reason in the decrease of basic strength with metal addition.

GasChrom MP-1 used to separate analytes has low affinity to water. For this, only low levels of water in organic solvents or organics in water can be analyzed by GasChrom MP-1 [43]. The latter one applies here, and due to huge fluctuations in the areas of water peaks results of water analyses were not taken into account. As only ethanol dehydrogenation is occurring in the reactor, what comes in as water should leave without being consumed. On the other hand, ethanol and water are sent in a 1:3 mole ratio as liquid to the system. Analyses of the gaseous phase obtained at “no reaction” temperature of 200°C for all catalysts showed that this ratio was in fact smaller. This can be attributed to the erroneous water peaks and it can be assumed that the mole ratio in the liquid phase was retained also in the gaseous phase.

No reproducibility experiments were carried out with fresh catalysts. However, used samples 1 and 6 were tested once again in the setup. Again only

acetaldehyde and hydrogen constituted the product distribution. As seen in Figures 11 and 12 there observed deactivation in both catalysts.

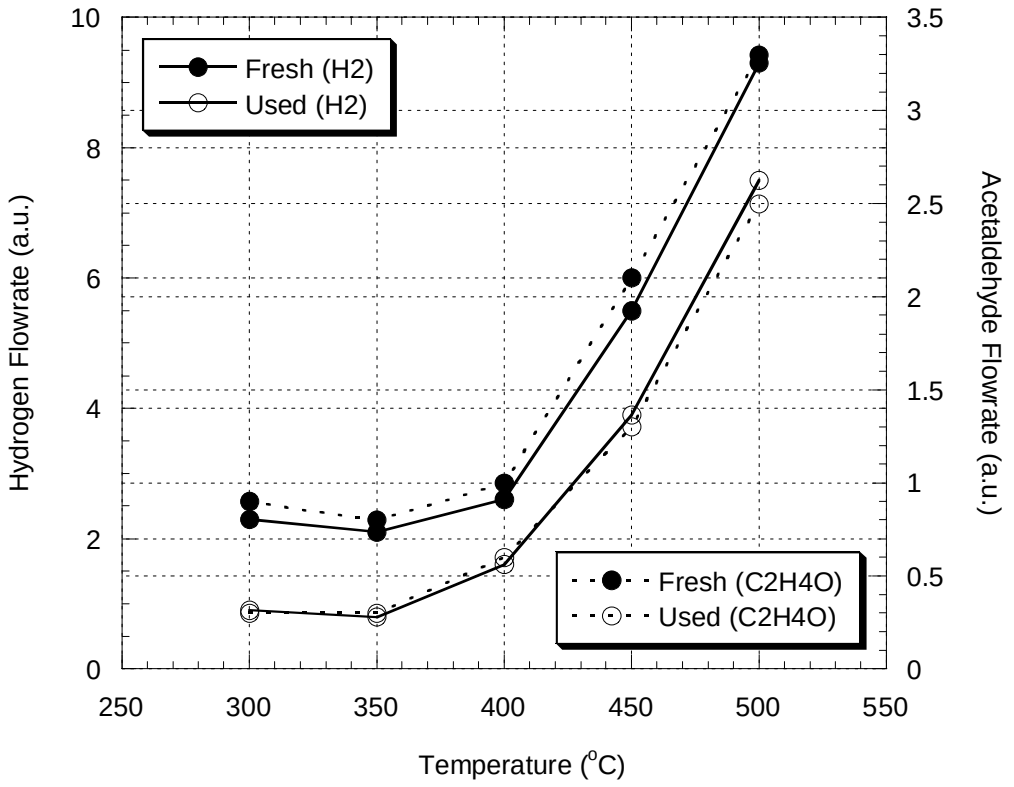

Figure 11. *Deactivation in sample 1 (EtOH:H_2O=1:3, GHSV~54000 cm^3/h-g catalyst, flow rate~90 cm^3/min. Mass of catalyst=0.1 g.)*

Figures 9-12 were drawn without using any calibration data. They were simply plotted considering hydrogen and acetaldehyde peak areas obtained in the analyses of the gas syringe samples, and processing those data with the argon areas to take the effect of the change in the flow rate, as reaction temperature increases, into account. This way, separate scales of arbitrary units were obtained for each species. When the data were to be further processed with the

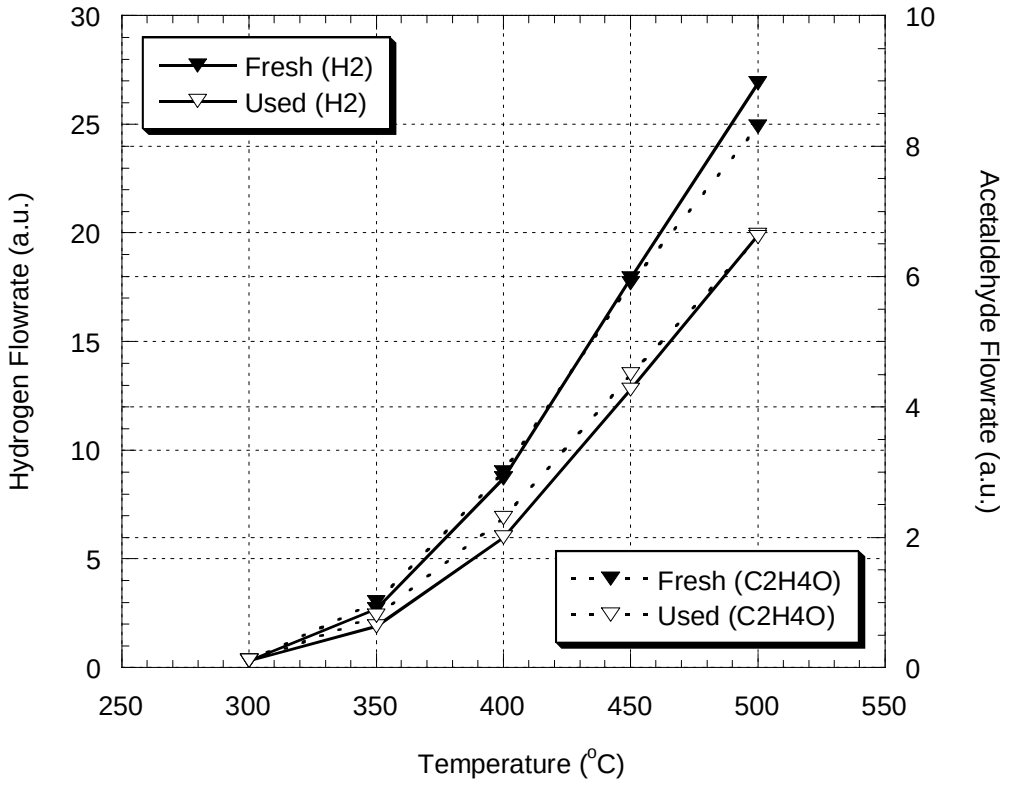

Figure 12. *Deactivation in sample 6 (EtOH:H_2O=1:3, GHSV~54000 cm^3/h-g catalyst, flow rate~90 cm^3/min. Mass of catalyst=0.1 g.)*

calibration data, however, somewhat mistaken results would arise. Calibrations of gases, H_2, CH_4, CO_2 and C_2H_4 were done using *another* setup by gas syringes, and of C_2H_4O, C_2H_6O and H_2O, by liquid syringes of *micro*liters. It is, therefore, very probable to arrive in incorrect figures after calculations using all calibration data together. Nevertheless, hydrogen flow rates of Figure 9 were re-plotted also using such calibration data as seen in Figure 13. Figure 13 is different from Figure 9. This shows that calibration appears as one of the major contributors, if there is any other, to the erroneous results. That is why, no completely-processed counterparts of Figures 9-12 will be given here.

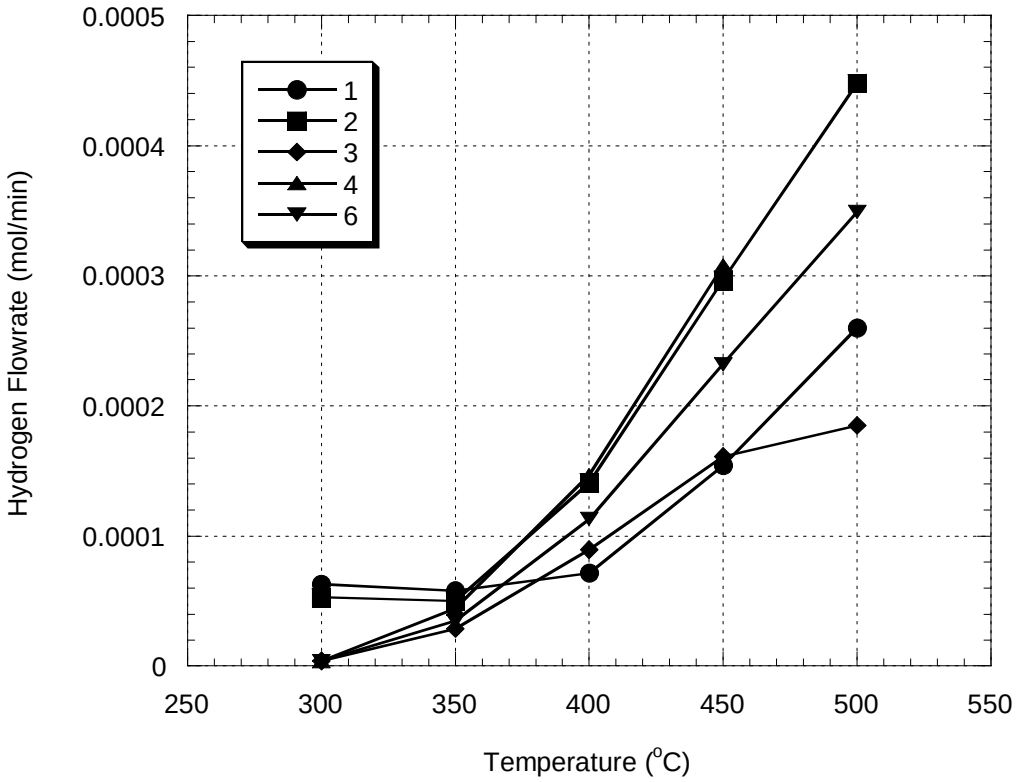

Figure 13. *Effect of calibration data on hydrogen flow rate data*

All calibrations were carried out again and again with each experiment as also indicated in the sample experiment schedule available in Appendix F. Yet, all these data can be collected and evaluated by means of some statistical tools, and an *averaged* calibration data for each species can be obtained. These data relate peak area of one component directly to its flow rate (mol/min) at the reactor exit. Further information on this calculation is given in Appendix E. Figure 9 was drawn once again after manipulated with this averaged calibration data as seen in Figure 14.

Figure 14 is much similar to Figure 9 except with the plot of sample 6. So, averaged calibration data can be used for the complete evaluation of the flow data.

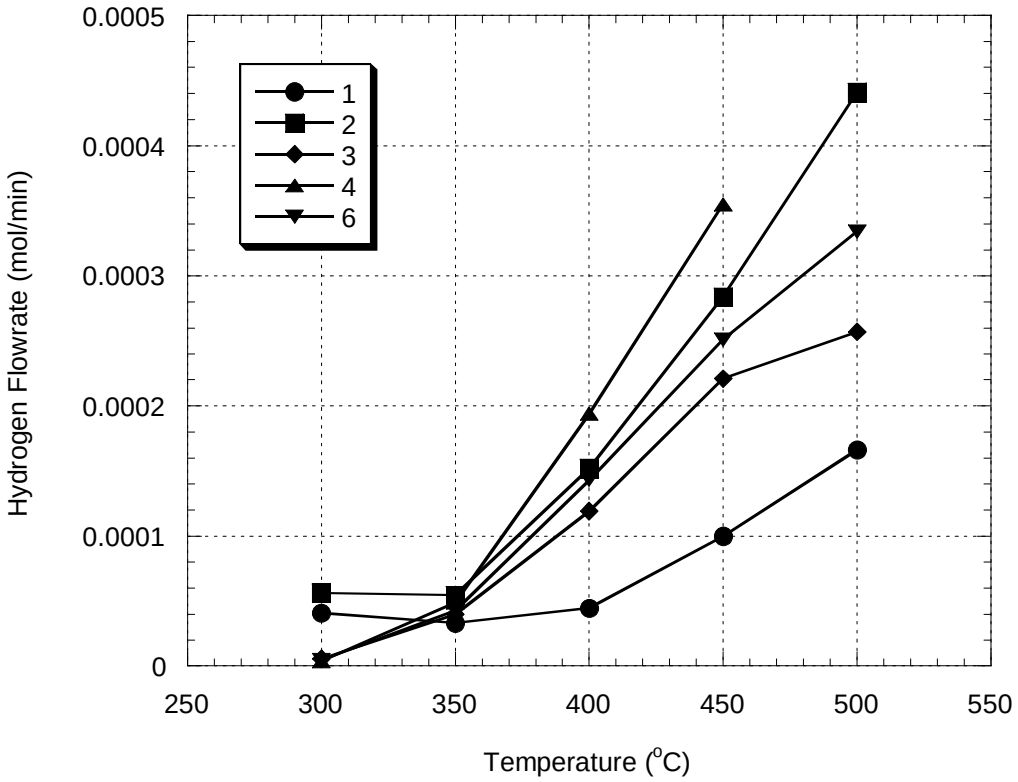

Figure 14. *Hydrogen flow rates re-plotted using averaged calibration data*

Figure 15 shows the results of the time-on-stream test carried out for sample 1 at 500°C for about 48 hours, which were evaluated by averaged calibration data. As seen in Figure 15 there is a continuous decrease in ethanol flow rate. While this experiment was running it was also observed that the decrease in the ethanol-water level in the cooler of the feeding unit (Figure 6) was decreasing by time. These two observations indicate that the peristaltic pump cannot pump the same amount of liquid as time passes which is most probably due to continuous treading of the rollers on the capillary tubing. Yet, as also seen in Figure 15, this does not have much significant effect on the flow rates of hydrogen, acetaldehyde, methane and ethylene as long as there still exist some ethanol in the reacting stream. Several studies in the literature [31-33] have reported a decrease in ethanol conversion which did not affect the selectivities of

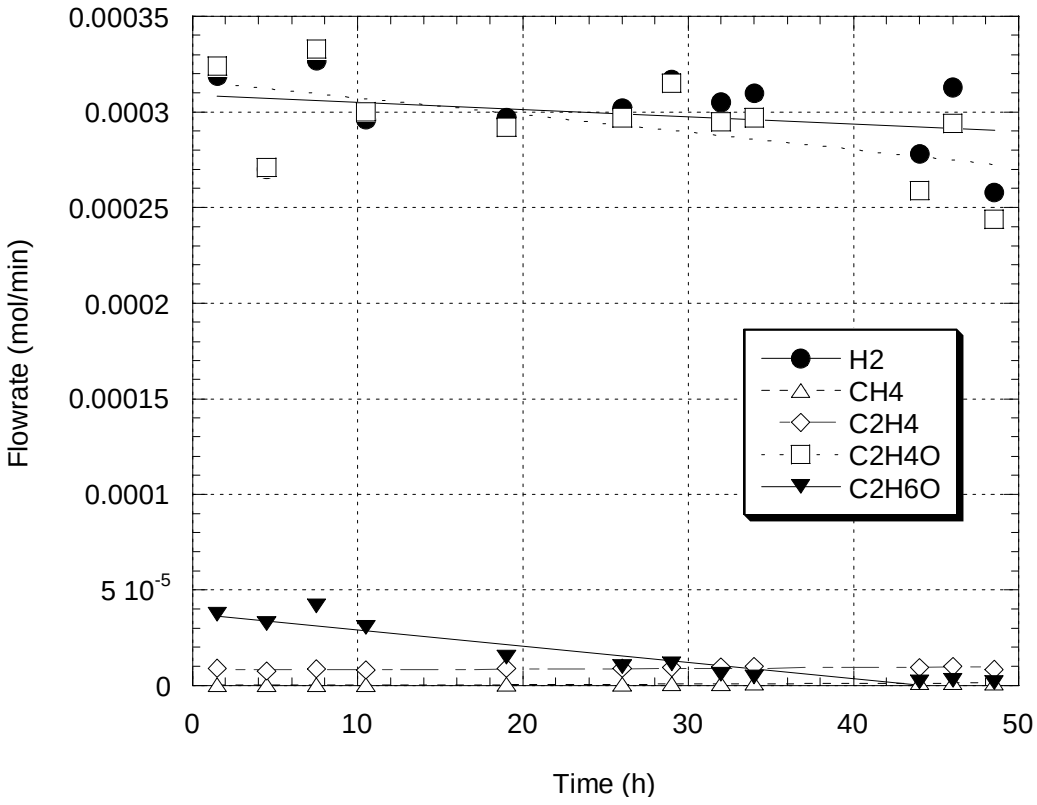

Figure 15. *Time-on-stream test of sample 1 at 500℃ (Lines shown are linear curve fits.)*

the products during time-on-stream tests of different catalysts. The situation here is not fully same with what has been described in those studies. Firstly, a decrease in ethanol conversion means an increase in its exit flow rate, and here, it is just the opposite. Secondly, unaffected selectivities do not always mean that the total flow rate of the products keeps constant. Decrease in the flow rates of the reactants decreases productivity, but at the same time, this also decreases the space velocity which promotes productivity. Therefore, unaffected flow rates or selectivities of hydrogen, acetaldehyde, and other minor products in the time-on-stream test can be attributed to this cancellation effect. On the other hand, almost constant flow rates of Figure 15 indicate that, contrary to what has been discussed on Figures 11 and 12, there is no catalyst deactivation on-stream.

Assuming similar behavior in the pumping of the liquid feed to the system in every experiment, the data of the previous experiments are still comparable. This can be seen in the hydrogen and acetaldehyde flow rates obtained by samples 4 and 6, which are almost equal at each temperature, as seen in Figures 9 and 10, respectively. This was an expected result as the compositions of those catalysts do not differ from each other. Decrease in the ethanol-water amount fed to the system, however, indicates a decrease in the space velocities as mentioned above. So, calculated space velocities were not, or at least, might not be what were obtained at the end of the experiments. It is expected to gain a higher selectivity towards hydrogen under lower space velocities; therefore, flow rates of the products at higher temperatures shown in the previous figure may appear to be higher than what should be under *calculated* space velocities[7].

Due to the discussion above no explicit ethanol conversion plots and no explicit hydrogen selectivity plots were given here, as Figures 9 and 10 already give an insight to them.

Elemental carbon balance was also carried out for all experiments done using both same-day calibration data and averaged calibration data. Carbon in the carbon-containing species at the reactor exit at every temperature is compared with the carbon in the ethanol exiting the reactor at 200°C, the no-reaction temperature. Percent errors in carbon balances are given in Table A.6 in Appendix D. A positive figure can be expressed as a "carbon *consumption* or accumulation," and a negative figure as a "carbon *generation*."

More positive values at higher temperatures would befit to the previous discussions as ethanol pumping rate is known to decrease with time (or, here, temperature) and as a possible coking action would result in a carbon accumulation. However, Table A.6 presents a set of data which is just the opposite. One reason of this can be a possible distillation effect in the bulb of the

[7] All steam reforming tests were done by increasing the reactor temperature after completing analyses in one temperature.

feeding unit which causes more water to go into reactor at the beginning of the experiments. Yet, this was proved to be irrelevant by the ethanol decrease of Figure 15[8]. As it was also observed almost equal hydrogen and acetaldehyde flow rates in the time-on-stream test, the only reason left can then be the incorrect calibrations of ethanol, which is one of the two major carbon-containing species other than acetaldehyde, done by using liquid syringes of microliters.

4.2.2. Autothermal Reforming

Autothermal reforming experiments were done with samples 2 and 3 of Set I, and with the Set II catalyst, sample 7. Again, flow rates and compositions of both liquid and gaseous phases of the reacting medium are given in Table 8. Again, 0.1 g catalysts were used in the experiments. Calculated space velocities for Set I catalyst tests remained the same as given in §4.2.1. For sample 7, however, two different tests were performed, one with high space velocity, and one with low space velocity. For the former test, space velocity was kept almost same with all previous experiments, 52000 cm^3/h-g catalyst which corresponds, however, to 20000 h^{-1} due to high packing volume[9]. Low space velocity, on the other hand, equals to 31000 cm^3/h-g catalyst (12000 h^{-1})[10]. These are all calculated values, and as shown in the previous section, they do not remain same throughout the whole experiment and, unfortunately, decrease.

Results showed that presence of oxygen in the reacting stream changed the product distribution a little bit by adding three more products. Analyses of the condensates collected in the condenser for disposal purposes showed that two of those species are in liquid phase under room temperature. Unfortunately, those species could not be identified. On the other hand, traces of species like diethyl

[8] So, the assumption of same gaseous composition with that in liquid is still valid.
[9] Corresponding to space time of 0.07 g catalyst.s/cm^3 or 0.18 s.
[10] Corresponding to space time of 0.12 g catalyst.s/cm^3 or 0.3 s.

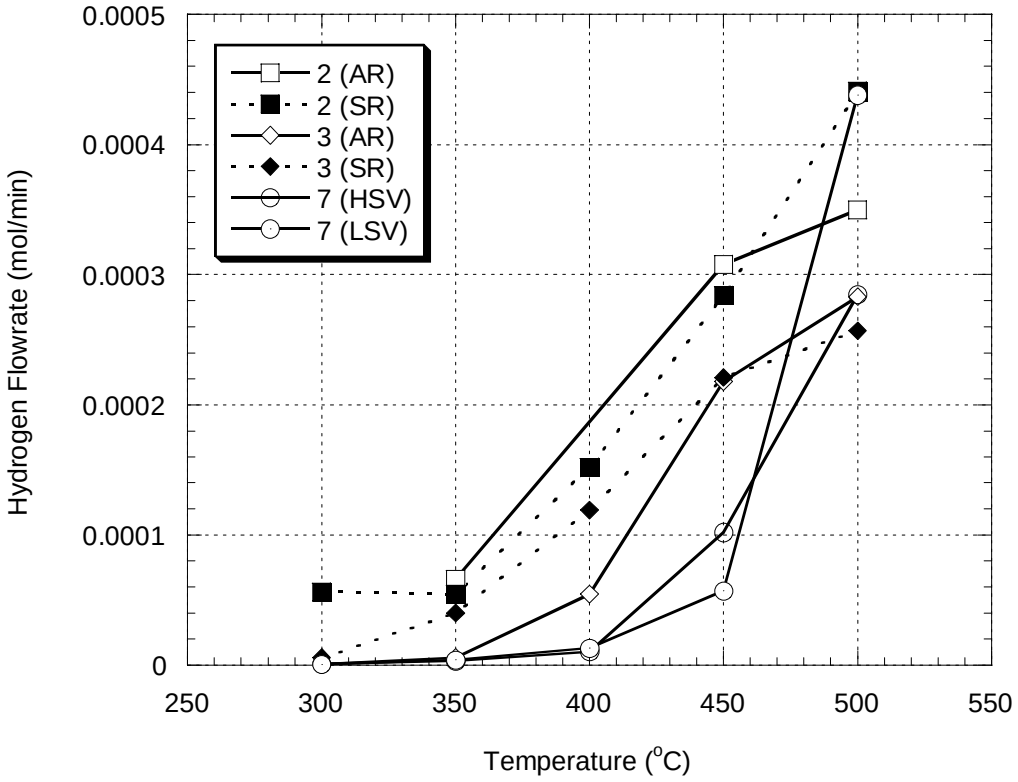

Figure 16. *Effect of temperature and catalyst on hydrogen flow rate (AR: Autothermal Reforming. SR: Steam Reforming. HSV: AR with high space velocity. LSV: AR with low space velocity. Calculated parameters: EtOH:H_2O=1:3; GHSV~54000 cm^3/h-g catalyst (SR, AR, HSV) ~31000 cm^3/h-g catalyst (LSV); flow rate~90 cm^3/min (SR) ~86 $cm^{3/}$min (AR, HSV) ~51 cm^3/min (LSV). Measured parameters: Mass of catalyst=0.1 g.)*

ether, ethyl acetate, ethane, acetic acid, acetone or formaldehyde reported in the literature were not observed.

As there were some major unidentified peaks in the analyses, it would be appropriate to present the results of the experiments in a fashion done in the previous section. Figures 16 to 20 illustrate the exit flow rates of hydrogen, acetaldehyde, methane, carbon dioxide and ethylene, respectively, obtained over

each catalyst[11]. Those of steam reforming tests done over samples 2 and 3 were also included in the figures for comparison purposes. It is worth noting that all data were evaluated using averaged calibration data of the previous section as argon could not be used for total flow rate determinations as mentioned in §3.3. Yet, analyses of oxygen could not be done properly either as the thermal conductivity of the reference gas, nitrogen, is near to that of oxygen.

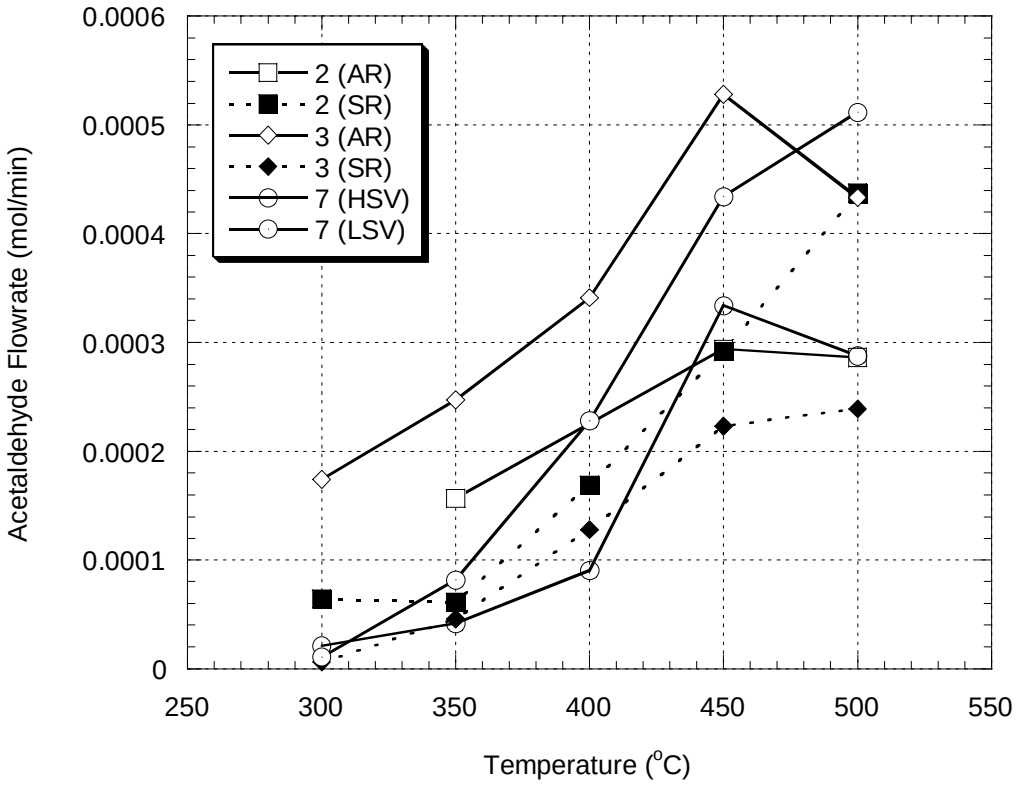

Figure 17. *Effect of temperature and catalyst on acetaldehyde flow rate*[11]

It is interesting that no carbon monoxide was produced in the experiments. Although none of the catalysts show a specific trend as seen in the figures, it is

[11] Experimental conditions and explanations to abbreviations used are given in Figure 24.

also strange enough to observe higher acetaldehyde flow rates compared to hydrogen. Acetaldehyde flow rates would be expected to be lower since acetaldehyde usually acts as an intermediate in the production of hydrogen. This is most probably a consequence of evaluation of raw data with the averaged calibration data as it is very unlikely for hydrogen to take place in the formation of larger molecules, maybe one or more of those unidentified species. As no carbon monoxide was also produced effect of water-gas shift reaction is eliminated. Therefore, it is reasonable to compare the catalysts on the basis of each species produced as done in Figures 16-20.

As seen in Figure 16, steam reforming over samples 2 and 3 still gives higher hydrogen productivity except for authermal reforming of sample 2 which seems to be better. Both high space velocity and low space velocity experiments of

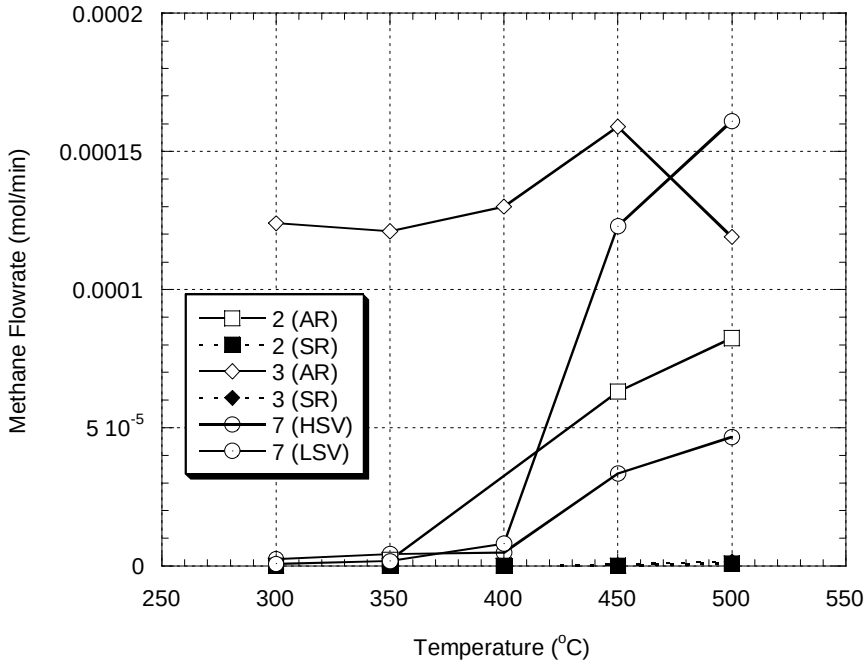

Figure 18. *Effect of temperature and catalyst on methane flow rate*[11]

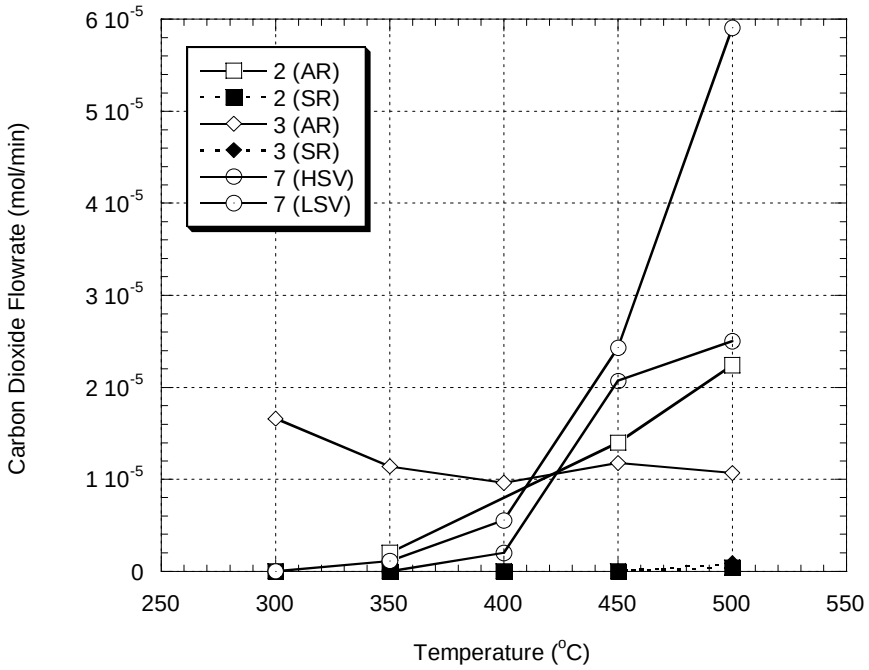

Figure 19. *Effect of temperature and catalyst on carbon dioxide flow rate*[11]

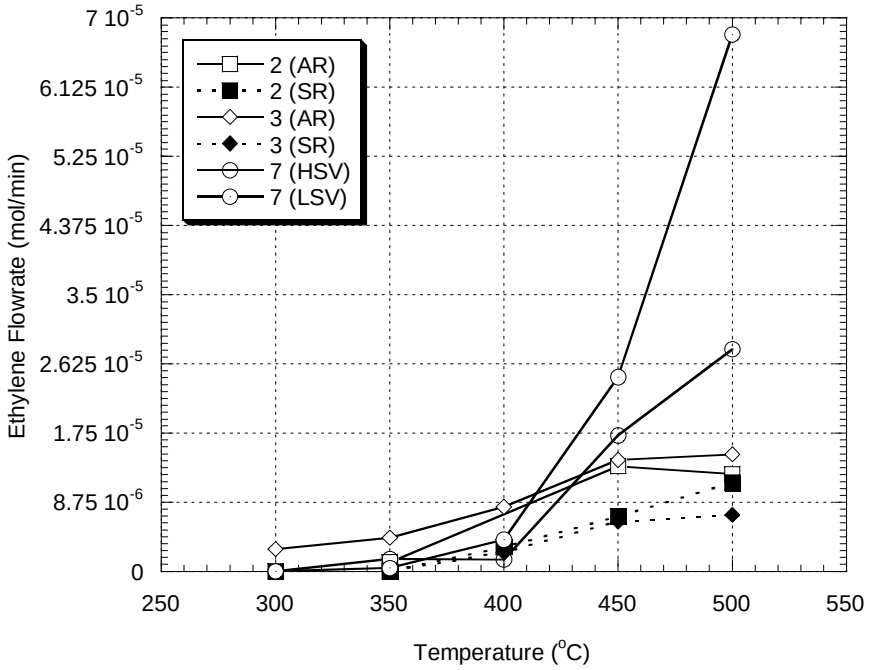

Figure 20. *Effect of temperature and catalyst on ethylene flow rate*[11]

cobalt catalyst, however, showed the poorest selectivity towards hydrogen. Yet, higher hydrogen flow rates were obtained when running with low space velocity.

On the other hand, formation of ethylene, methane and carbon dioxide increased with the presence of oxygen. Cobalt catalyst showed higher productivity towards ethylene and carbon dioxide. Moreover, by decreasing the space velocity higher flow rates for all products were obtained over the cobalt catalyst. Here, it is worth noting that experiment for low space velocity cobalt testing was started at 500°C and ended up at 200°C.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Decrease in the fossil fuel reserves on which more than 85% of world's energy depends on today, and new regulations brought on emission control have led the way to studies on alternative fuels. Hydrogen production through ethanol steam reforming is one such new research area.

ZnO catalysts are known as methanol synthesizing catalysts from syngas, hydrogen and carbon monoxide. From the principle of microkinetic reversibility, catalysts promote also backward reaction as they promote forward reaction. Starting from this point, it may be possible to produce hydrogen with high selectivities from methanol and even ethanol over ZnO catalysts.

Ethanol is a renewable feedstock. According to studies available in the literature when ethanol is reformed with steam over suitable catalyst, hydrogen can be produced with carbon dioxide; however, no additional carbon dioxide is emitted to the atmosphere, and instead, carbon in ethanol is only recycled in nature to be used again in photosynthesis.

In the first part of this study, ethanol steam reforming reaction was tested over sol-gel-prepared non-promoted, and Pd- or Cu-promoted zinc oxide catalysts supported on silica in a developed experimental setup. Analyses showed similar results with those in the literature. These catalysts acted as ethanol dehydrogenation catalysts in the temperature range of 300-500°C and under other experimental conditions. Hydrogen selectivity was higher over non-promoted catalysts at high temperatures and over Cu-promoted ones at low temperatures. Pd and Cu promotion would be expected to bring superiority to

ZnO catalysts; however, it didn't come out to be so. The reason of this can be attributed to the presence of possible zinc silicates and metal zincates enclosed in closed pores which are not reachable to adsorbed gas molecules. These closed pores can also be the reason in the decrease in BET surface area and basic strength with metal addition to the catalyst.

Deactivation due to air contact was observed when used catalysts were tested once again later in the setup. On the other hand, there was no deactivation on-stream.

It was further detected that selectivities were not affected much by the decrease in ethanol and water amount in the reacting medium as long as there exist some.

In the second part of the study, steam reforming experiments were carried out this time with the presence of oxygen or air over those promoted zinc oxide catalysts and over SBA-15-supported cobalt catalyst. These autothermal reforming tests showed similar hydrogen selectivities over promoted zinc oxide catalysts when compared with their steam reforming results. On the other hand, hydrogen selectivities were lower over the cobalt catalyst. Formation of side products like methane, carbon dioxide, ethylene, and three more species which could not be identified increased in autothermal reforming experiments.

Formation of carbon monoxide was not seen in any of the experiments.

CHAPTER 6

RECOMMENDATIONS

As mentioned previously, setting up a proper feeding unit and trying to establish a working experimental system took about three fourth of the time spent on this study as dealing with three-phase systems is not an easy task. Still, results of the experiments revealed the problems existing with the feeding unit due to changing pumping rate of the peristaltic pump. A syringe pump could have been used instead of a peristaltic pump in the setup to obtain a steady feeding.

On the other hand, carrying the analytes to GC in a gas syringe was not an easy task either. First of all, before taking samples from sampling vessel into the syringe, syringe was heated by a heating gun not to let any condensation to happen within the syringe. This was something reducing the lifespan of the syringe as heating may harm the Teflon structures. So, one should be as quick as possible not to lose time while taking the sample and injecting it to GC. Secondly, the injection port of the GC was equipped with a septum as the sampling vessel, and septum particles were, most of the time, blocking the needles of the syringes. Trying to take those particles out of the needle was something annoying and time consuming as it was causing termination of the experiment to delay. For this, analytes should have been sent to GC on-line instead of by using syringes. However, this time the line from the reactor to the injection port of the GC would need to be surrounded by a longer heating tape or by extra heating tapes which was not possible due to unavailability.

A longer column had to be used, and low flow rates along with a temperature ramp had to be applied in GC in order to separate species like hydrogen, carbon monoxide, methane and carbon dioxide which come out of the column rather

quickly while trying to decrease the retention time of the final component, ethanol, as much as possible. As a result of this, one analysis lasted for about 1 hour. For this, analysis time was the major reason in having *long* experiments usually lasting for more than one day. Incorrect injections due to condensation in the syringe or plugged syringe needle also caused additional delays.

On the other hand, the most unpleasant situations occurred when the electricity was cut. Many analyses and experiments were terminated as a result of electricity cuts. For this, laboratories should be equipped with generators as sudden voltage changes not only terminate the experiments but also give harm to expensive equipments like GCs.

Analyses of autothermal reforming experiments could not be carried out completely as argon used as the total flow determinant could not be separated from oxygen in the column. Sending helium instead of argon would not solve the problem either as this time helium, hydrogen and carbon monoxide would not be separated. Changing the reference gas of the GC to helium and using nitrogen in the setup both as the carrier gas and the internal standard would not be effective also since hydrogen would not be analyzed properly due to very near thermal conductivities with the reference gas, helium. The only solution could be a concurrent analysis in another GC.

Finally, a more practical method needed to be used for calibration as the major contributor to erroneous results was shown to be the calibration data. For instance, a volumetric calibration of feed and products could have been carried out in which volumetric decrease in the ethanol-water solution of the cooler with time could have been recorded, and several sets at the “no-reaction” temperature could have been carried out. This way, ethanol could have been more accurately calibrated.

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APPENDIX A

ECONOMIC ANALYSIS

Theory

An economic analysis was carried out for a system consisting of an ethanol steam reformer and a proton exchange membrane fuel cell (PEMFC).

Figure A.1 shows a schematic representation of a PEMFC. Hydrogen from the reformer is fed to the anode of the fuel cell, and pure oxygen or air is fed to the cathode. An electron flow takes place in the external circuit as a consequence of the anodic and cathodic reactions, which is nothing but electricity.

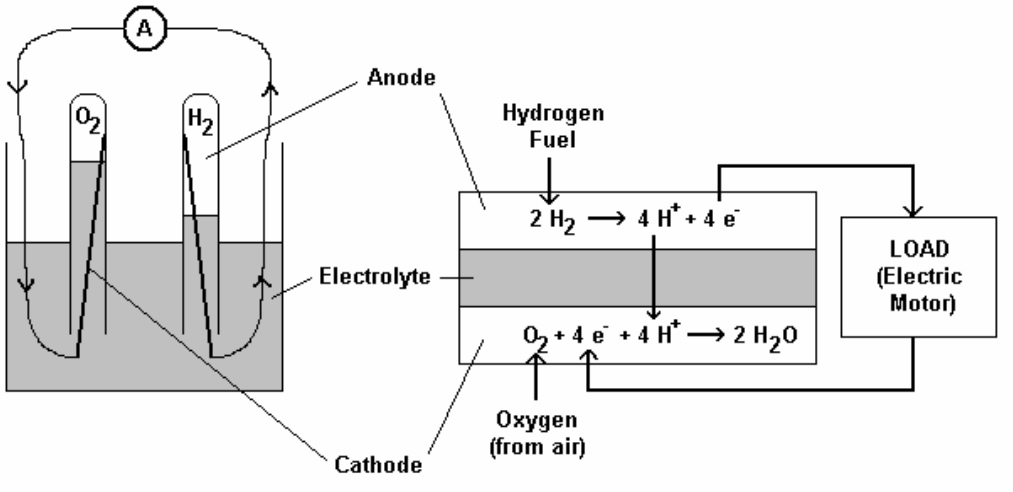

Figure A.1. *Proton exchange membrane fuel cell (PEMFC)*

Studies available in the literature have shown that it is possible to obtain almost complete conversions in ethanol steam reforming with very high hydrogen selectivities at elevated temperatures. Therefore, at the very beginning of the analysis it was assumed that complete reaction to carbon dioxide and hydrogen was taking place in the reformer of the system. Reactants, ethanol and water of the reformer, and air of the fuel cell, were then assumed to be fed to the system at room temperature. Operating temperature of PEMFC was further assumed to be 75°C which is a typical value. Temperature of the effluent from the reformer leaving at a high reforming temperature should then be lowered to 75°C. Therefore, it is reasonable to assume for the steam reforming as taking place at 75°C since heat necessary to increase the temperature of ethanol and water in the reformer high above 75°C would well be gained back while lowering the temperature of carbon dioxide and hydrogen to 75°C.

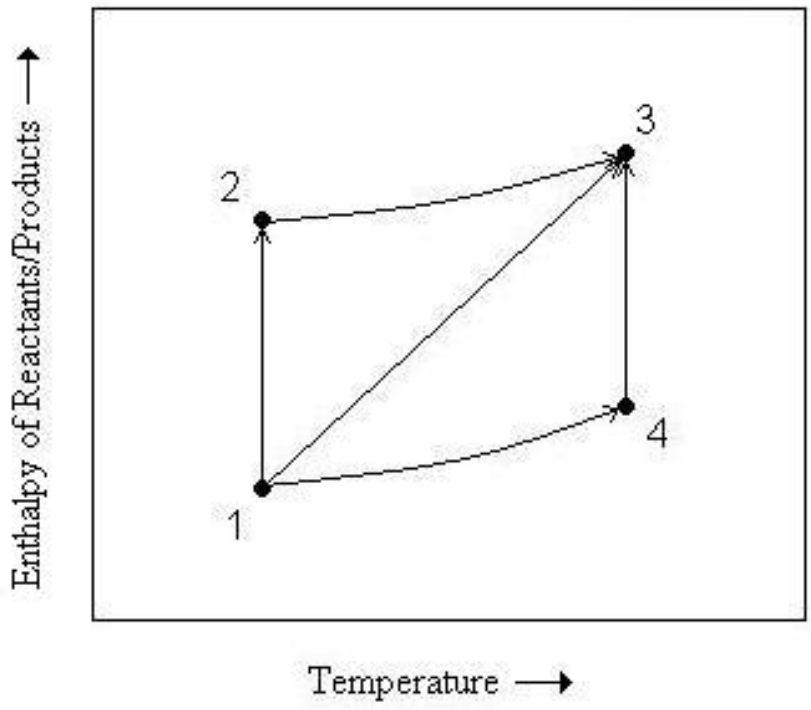

Figure A.2. *Enthalpy-temperature diagram*

Figure A.2 shows a representative enthalpy-temperature diagram for reformer reactants and products. Ethanol steam reforming is an endothermic reaction; therefore, points 1 and 4 represent heats of reactants at 25°C (room temperature) and at 75°C, respectively. Similarly, points 2 and 3 represent heats of products again at 25°C and 75°C, respectively. In the reformer, ethanol and water are firstly heated to 75°C at which temperature, then, complete reaction takes place, as shown in the figure by the path from 1 to 3. Calculations can be carried out also by following the path from 1 to 4, and then, the path from 4 to 3. Therefore, in the analysis, reaction heat of ethanol steam reforming at 25°C, and sensible heats of carbon dioxide and hydrogen, and also of air, necessary to increase their temperature from 25°C to 75°C were used. Values of reaction and sensible heats are listed in Table A.1.

Table A.1. *Reaction heat and sensible heats used in the analysis [44]*

Heat of reaction at 25°C (kJ/mol)	$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$		
	173.5		
Sensible heat to raise temperature from 25°C to 75°C (J/mol)	CO_2	H_2	Air
	1907	1443	1458

To relate the voltage of the fuel cell to its current density, on the other hand, the equation available in the publication by Larminie and Dicks [45], which brings together all the irreversibilities in the fuel cell like fuel crossovers, ohmic loses, etc., was adapted:

$$V = E - (i + i_n)r - A\ln\left(\frac{i + i_n}{i_0}\right) + B\ln\left(1 - \frac{i + i_n}{i_1}\right) \tag{27}$$

where, E: reversible open circuit voltage,

i_n: internal and fuel crossover equivalent current density,

A: slope of the Tafel line,

i_0: either exchange current density at the cathode if the cathodic overvoltage is much greater than the anodic, or a function of both exchange current densities,

B: constant related to mass transfer overvoltage,

i_l: limiting current density at the electrode which has the lowest current density,

r: area specific resistance.

Typical values for the constants of this equation were also taken from the same source as listed in Table A.2.

Table A.2. *Typical constants in equation (27) for PEMFC [45]*

Constant	Typical value for PEMFC
E (volt)	1.2
i_n (mA/cm^2)	2
R (kΩ/cm^2)	30×10^{-6}
i_0 (mA/cm^2)	0.067
A (volt)	0.06
B (volt)	0.05
i_l (mA/cm^2)	900

Ethanol and electricity costs were taken from Peters and Timmerhaus [46]. Table A.3 lists the values of them. On the other hand, heat is always generated in

a fuel cell. In this analysis, the amount of heat which was calculated by the following equation [45] was considered as electricity and included in the analysis as a "money gained:"

$$Heating\ rate = n\,I\left(1.25 - V_c\right) \tag{28}$$

where, n: number of cells in the fuel cell,

I: current,

V_c: average voltage of one cell.

Table A.3. *Ethanol and electricity costs [46]*

Item	Cost
Ethanol	$2/gal
Electricity	$0.035-$0.13/kWh

It was presumed that water vapor was finally produced in the fuel cell. However, nothing further about this steam was taken into consideration in the analysis. Moreover, no purchase cost or no purification cost for water fed to the reformer was taken into account.

Each calculation in the analysis was done against a current density of the fuel cell. For a specific electrode area, current, and then via equation 27, fuel cell voltage, and hence, the amount of electricity produced were calculated. Heat generated in the fuel cell was then obtained from equation 28. Altogether these figures sum up as the total money earned at the end. To calculate the operating

cost, or in other words, the total money spent, hydrogen fuel usage was calculated using the following formula:

$$Hydrogen\ usage = \frac{I}{2F} \tag{29}$$

where, I: current,

F: Faraday constant.

From this value, amounts of ethanol and air used in the system were obtained through reaction stoichiometries. Finally, ethanol cost together with sensible heat costs and reaction heat cost gave the operating cost.

Same analysis was also carried out for ethanol autothermal reforming. Again complete conversion was assumed to carbon dioxide and hydrogen. Different from steam reforming case, autothermal reforming also uses oxygen in the reformer. So, it was assumed that air was also fed to the reformer as the oxygen source. However, then, sensible heat change of nitrogen in the reformer was included in the calculations as well.

Results

Deluga et al. [7] made use of a perfect fuel cell assuming that hydrogen fed to the fuel cell is totally converted into steam and the exothermic heat of this process is totally converted into electricity in their economic analysis. Although there are studies reporting more than 95% ethanol conversion with very high hydrogen selectivity in a reformer as also taken to be so in the study of Deluga et al., there is no such perfect fuel cell. So, a more realistic analysis was carried out for ethanol steam reforming.

Figures A.3 and A.4 illustrate the results of the economic analysis carried out for one-hour operation of a reformer-fuel cell system equipped with a small

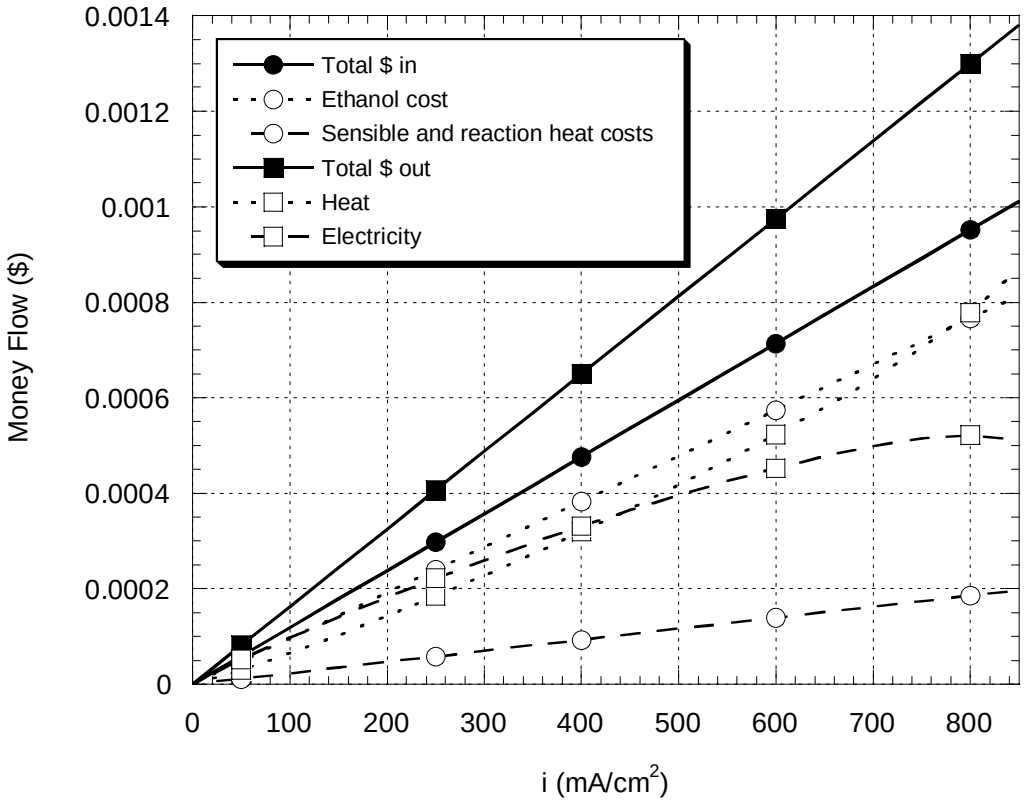

Figure A.3. *Money flow scheme for a system of an ethanol steam reformer and a small PEM cell of area 10 cm^2 (See text for details.)*

electrode having 10 cm^2 area. "Total $ in" stands for the money spent to operate the system. It is, in other words, the operating cost which includes the ethanol cost along with the sensible and reaction heat costs. Similarly, "Total $ out" is used for the amount of money earned at the end out of this system. This value comprises the heat generated in the fuel cell which is included as electricity, and the electricity produce by the fuel cell. Cost of electricity was taken to be $0.13/kWh.

As seen in the figures ethanol cost makes up most of the operating cost of the system which is due to the amount of energy used to remove all water content in

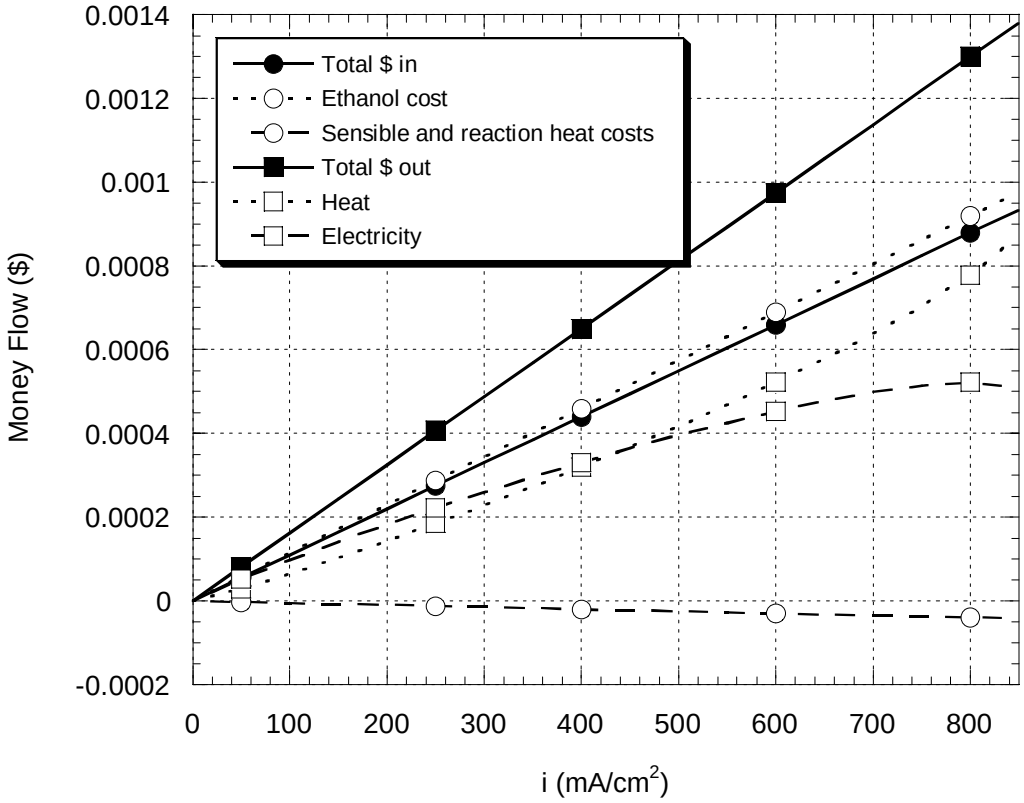

Figure A.4. *Money flow scheme for a system of an ethanol autothermal reformer and a small PEM cell of area 10 cm^2 (See text for details.)*

bioethanol to produce ethanol. On the other hand, heat generated in the fuel cell has an energy value that cannot be underestimated. When the "Total $ in" and "Total $ out" curves are compared, it is observed that a profit of about 37% and 48% can be made out of such a system using a steam reformer and an autothermal reformer, respectively. Interestingly, it has been shown by recent studies that the energy in the fuel ethanol is at least 1.34 times the energy used in its production which is quite near to the values obtained here [7]. Yet, however, to remain on the profitable side, electricity price/cost should not fall below $0.09/kWh for both reformers. At this value operating cost becomes almost the same as the selling price of the electricity at which point, though, operating such

a system would be meaningless. Therefore, the fuel cost at the end of this analysis came out to be $0.09/kWh which is more than twice of the fuel cost estimated by Deluga et al. [7]. Still, this value will decrease if bioethanol can be used instead of pure ethanol which can supply even more than the amount of water necessary to drive the steam reforming reaction.

One more point should be made clear: Figures A.3 and A.4 show the results for a cell of 10 cm^2 electrode. Increase or decrease in this value only shifts the curves up or down, respectively, unchanging the profit ratio since all calculations are linear multiplication of data.

APPENDIX B

CATALYST PREPARATION AND CHARACTERIZATION

Preparation of Set I Catalysts

Contents here were obtained from Assist. Prof. Dr. Erol Şeker and Işıl Tezel at Izmir Institute of Technology. This information is presented here for the completeness of the study.

Promoted and non-promoted ZnO catalysts supported on silica were prepared by a single-step sol-gel technique based on the technique of Brinker et al. [47]:

Table A.4. *Amounts used in preparation of Set I catalysts*

Species	Samples					
	1	**2**	**3**	**4**	**5**	**6**
Ethanol (ml)	4	4	4	4	4	4
TEOS (ml)	4	4	4	4	4	4
Water (ml)	0	0	0	1.519	1.519	2
HCl (1M) (ml)	.013	.013	.013	.02622	.0065	.013
NH_4OH (.05M) (ml)	.833	.833	.833	.833	.833	.350
$Zn(NO_3)_2.6H_2O$ (g)	3.7760	3.7792	3.7775	3.7740	3.7703	3.7750
$Cu(NO_3)_2.2H_2O$ (g)	.4637	.3321	0	0	0	0
$Pd(NO_3)_2.H_2O$	0	0	.1190	0	0	0

Tetraethylorthosilicate (TEOS) was firstly dissolved in ethanol. Temperature of the resulting solution was raised to 65°C, and diluted hydrochloric acid was added into the solution. Stirred continuously by a magnetic stirrer this solution was kept at 65°C in a vessel equipped with a total reflux for 3 hours. Meanwhile for the preparation of non-promoted catalysts, $Zn(NO_3)_2.6H_2O$ was dissolved in NH_4OH at 65°C. This basic solution was added into previously prepared acidic solution and stirred continuously at 65°C until gel formation was observed. In a similar manner, for the preparation of Cu and Pd promoted catalysts $Zn(NO_3)_2.6H_2O$ was dissolved in $Cu(NO_3)_2.2H_2O$ and $Pd(NO_3)_2.H_2O$, respectively, to prepare the basic solution which was then added into acidic solution until the formation of gel. Table A.4 summarizes the amounts used during preparation. Gels were then dried under vacuum for three days.

Preparation of Set II Catalyst

Set II catalysts were prepared at Chemistry Department of METU under the supervision of Assist. Prof. Dr. Ayşen Yılmaz. Information here was obtained from Burcu Akça and given here for the completeness of the study.

A triblock co-polymer, P123 ($EO_{20}PO_{70}EO_{20}$)[12], was dissolved in hydrochloric acid under continuous stirring by magnetic stirrer at room temperature for one hour. TEOS, as the silica source, and $CoCl_2.6H_2O$, as the cobalt source, were added into the mixture at 40°C. The resulting solution was again stirred continuously for about 20 hours until gel formation was observed. Then gels were dried overnight at 90-100°C, and filtered afterwards.

Catalyst Characterization

Calcination procedure of Set I catalysts was determined by means of TGA technique (DuPont 2000) in Chemical Engineering Department at METU.

[12] Triblock poly(ethyleneoxide)-poly(propeleneoxide)-poly(ethyleneoxide) co-polymer

Appendix C presents TGA data for samples 1, 3 and 5, and the calcination procedure performed for each Set I catalyst.

After calcination of Set I catalysts they were ground in mortar to 60 mesh size. On the other hand, Set II catalyst was calcined directly at 500°C for two hours and used without grinding.

BET surface areas and average pore diameters of some of SET I catalysts and Set II catalyst were determined by nitrogen adsorption in Coulter Omnisorp 100 at Izmir Institute of Technology and in Micromeritics ASAP 2000 at METU, respectively.

APPENDIX C

CALCINATION PROCEDURES AND TGA DATA OF SET I CATALYSTS

Table A.5. *Calcination procedures of Set I catalysts*

Sample	Calcination Procedure
1, 2, 4, 5, 6	*RT* [10°C/min] *150℃* (1h) [10°C/min] *350℃* (1h) [3°C/min] *450℃* (1h) [10°C/min] *500℃* (1h+3h[13])
3	*RT* [10°C/min] *150℃* (1h) [3°C/min] *200℃* (1h) [10°C/min] *350℃* (1h) [10°C/min] *500℃* (1h+3h[13])

[13] After one hour at 500°C, samples were weighed and kept for another 3 hours at 500°C after which samples were weighed once again. As there were no significant weight differences calcination of samples was completed.

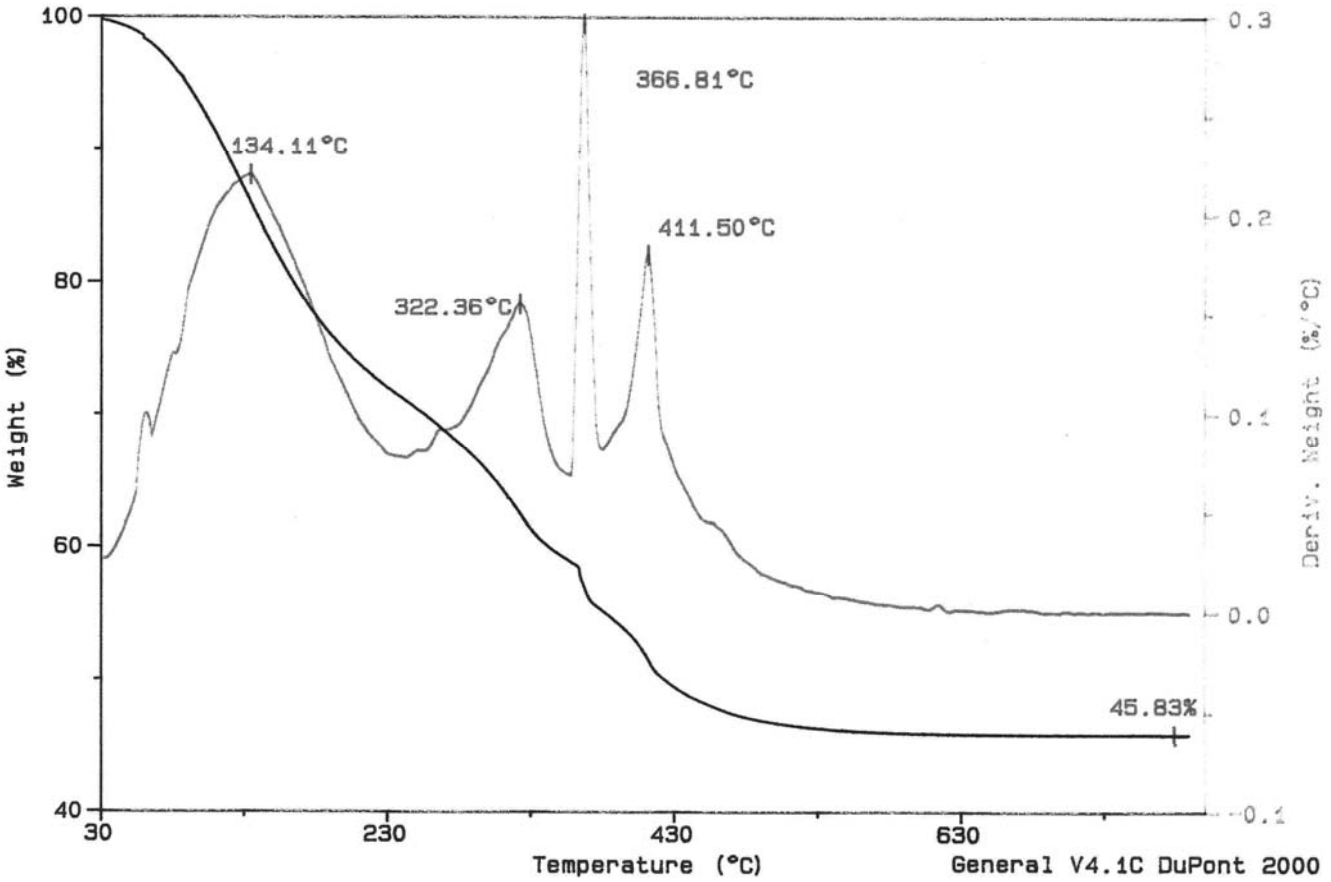

Figure A.5. *TGA of sample 1 (RT [10 ℃/min] 700 ℃. Air flow: 75 cm^3/min.)*

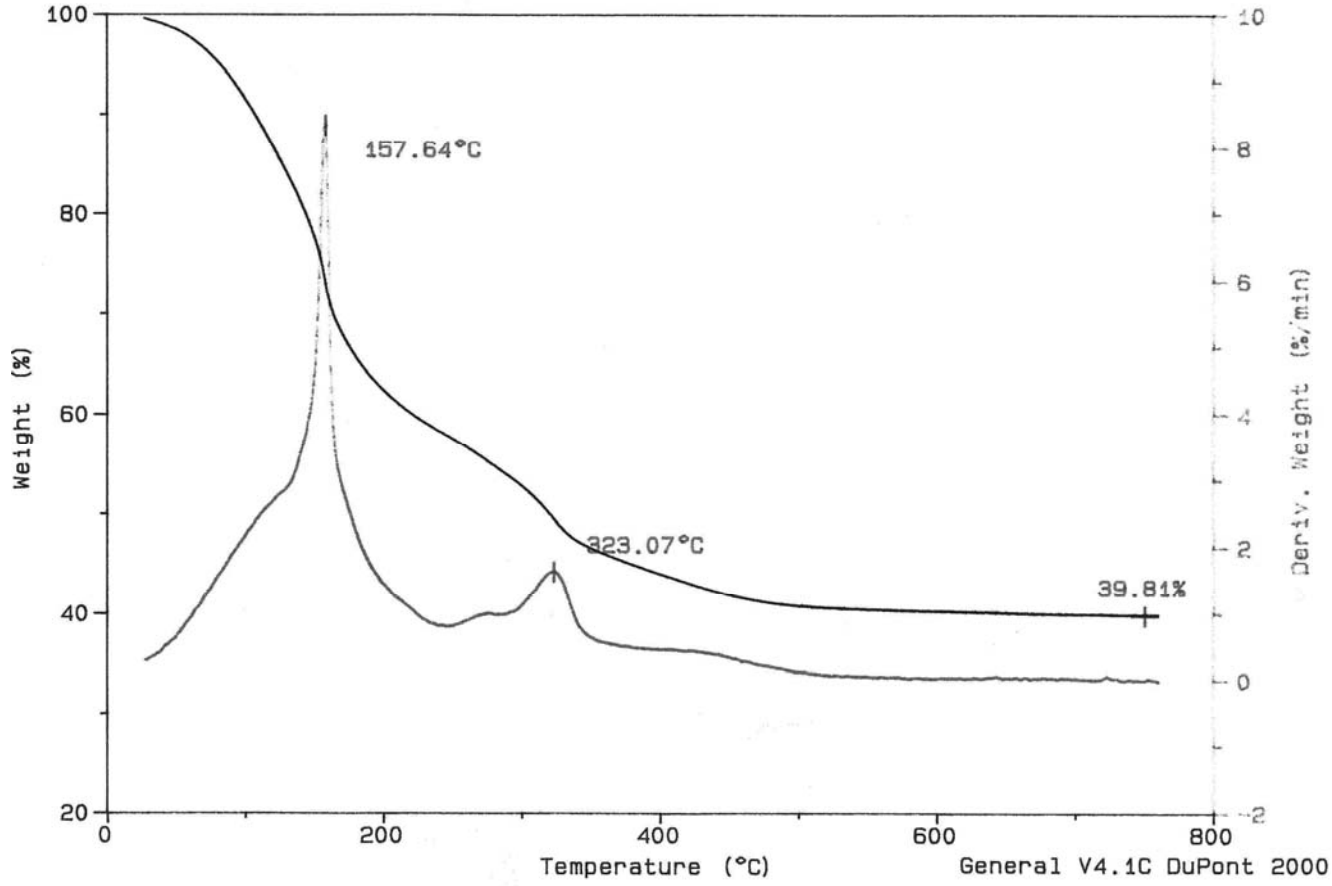

Figure A.6. *TGA of sample 3 (RT [10 ℃/min] 700 ℃. Air flow: 60 cm^3/min.)*

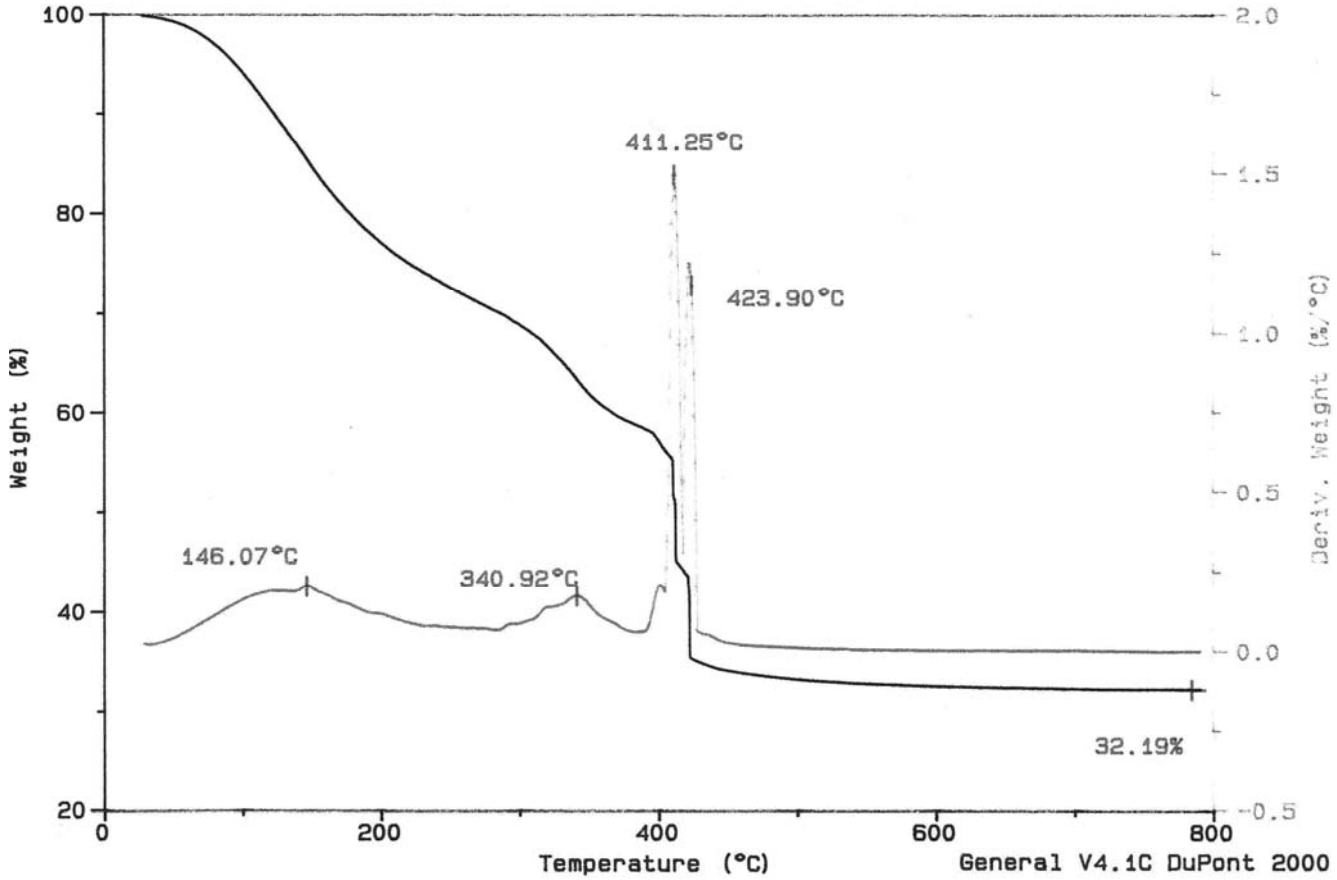

Figure A.7. *TGA of sample 5 (RT [10 ℃/min] 700 ℃. Air flow: 75 cm^3/min.)*

APPENDIX D

ELEMENTAL CARBON BALANCES IN STEAM REFORMING TESTS

Acetaldehyde and ethanol are the only carbon-containing species encountered in ethanol steam reforming experiments. Amount of ethanol, and thus that of elemental carbon, fed to the system was obtained from the analysis of the effluent obtained at the "no reaction" temperature, 200°C. This value was then compared with the amount of elemental carbon in other reaction temperatures.

Table A.6. *Percent errors in elemental carbon balances (Fresh catalysts. S: Same-day calibration data. A: Averaged calibration data.)*

Sample	T (°C) →	300	350	400	450	500
1	S	+5.9	+9.0	-11.5	-1.7	-3.9
	A	-9.3	+6.8	-25.1	-21.3	-22.8
2	S	+9.3	+15.7	-6.1	-10.1	-18.6
	A	+2.1	+7.1	-24.5	-27.1	-51.0
3	S	+12.4	+6.8	+14.0	+22.3	+32.5
	A	+12.4	+6.0	+11.5	+11.1	+19.5
4	S	-0.2	+0.4	-11.1	-5.1	N/A
	A	+27.9	+17.0	-15.8	-3.2	N/A
6	S	0	-10.0	-51.1	-89.0	-120.5
	A	-11.9	-15.4	-52.6	-49.2	-45.6

Results are summarized in Table A.6. A positive figure can be expressed as a "carbon *consumption* or accumulation," and a negative figure as a "carbon *generation*."

APPENDIX E

AVERAGED CALIBRATION DATA

For steam reforming experiments, peak areas of components were related to their corresponding flow rates through same-day calibration data obtained from argon areas (necessary for the determination of total gas flow rate) and single-point calibrations done for every component in each experiment. All such area-to-mol/min calibration data were collected and their slopes were calculated (area/flow rate). 95% confidence level intervals of those slopes were then computed from their average values and standard deviations. The area and flow rate data giving those slopes falling in that interval were selected, and from these data area-to-mol/min calibration curves were plotted. These plots are given in Figures A.8-A.13[14].

It should be carefully noted that these plots are not calibration curves obtained simply by sending a gas at some flow rate to GC and obtaining the peak area. First of all, they all include experimental data of steam reforming experiments which were quantified by single-point calibration and in which effect of temperature was included by argon peak area. Temperature affects the total flow rate, and hence, the argon area, in two ways: 1. If there were no reaction taking place, increase in temperature would accelerate the gas molecules. 2. There are reactions taking place differently at different temperatures so total flow rate will be different at each temperature[15]. Therefore, these data are termed as "averaged" in the text because they were obtained at five different experimental temperatures between 300-500°C and they were applied to every other raw data

[14] IS in figure titles stands for "internal standard" which is argon.
[15] Flow rate increased with temperature in steam reforming tests as two molecules were produced from one molecule of ethanol in the only reaction taking place, ethanol dehydrogenation.

(peak areas) which have no argon data disregarding the temperature. These plots are, thus, temperature-corrected calibration curves.

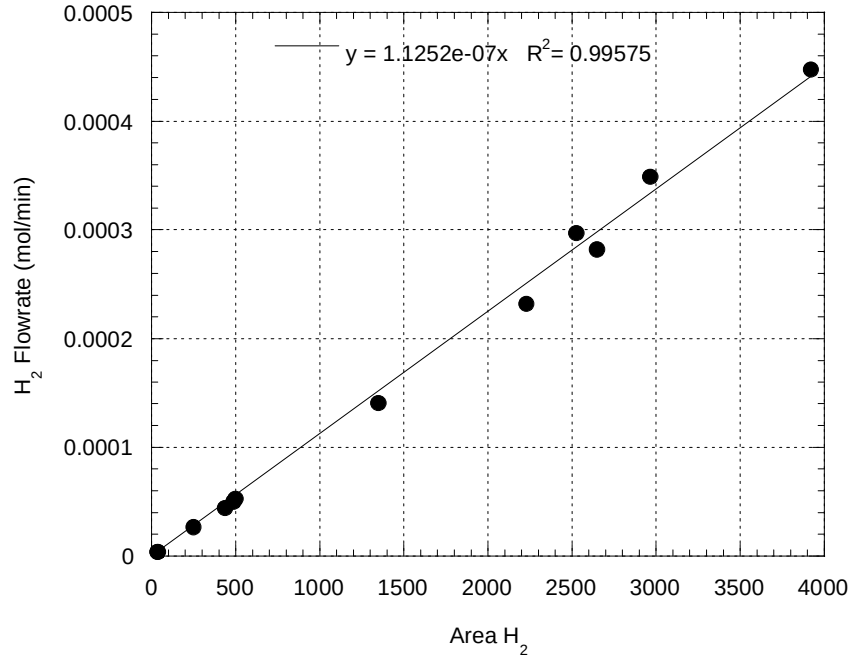

Figure A.8. *Effect of temperature on quantification of hydrogen via an IS*[14]

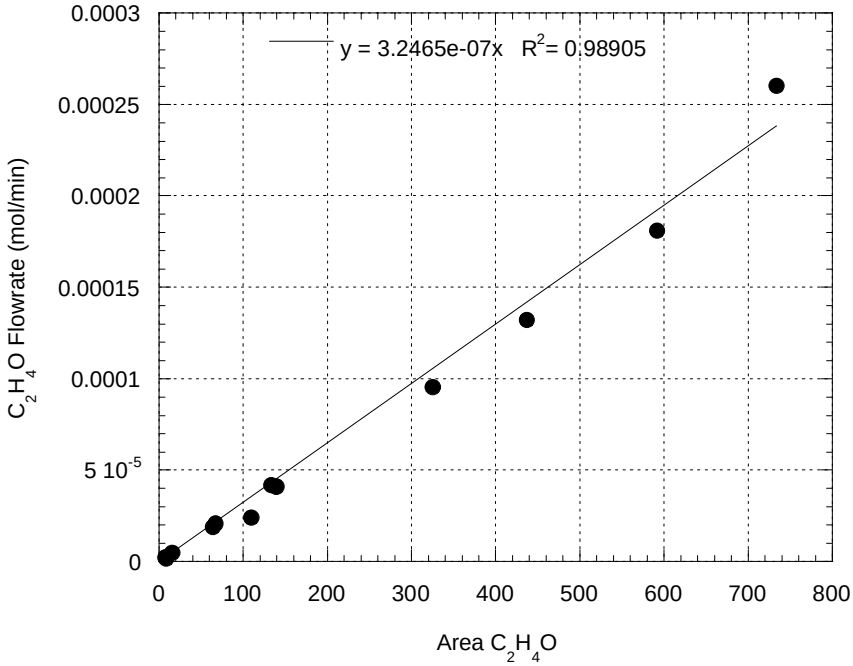

Figure A.9. *Effect of temperature on quantification of acetaldehyde via an IS*[14]

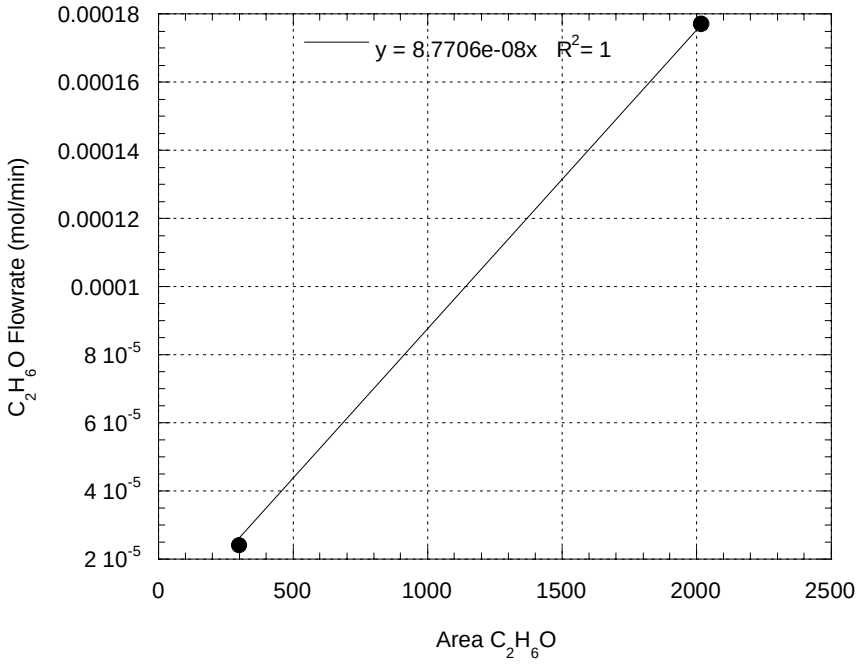

Figure A.10. *Effect of temperature on quantification of ethanol via an IS*[14]

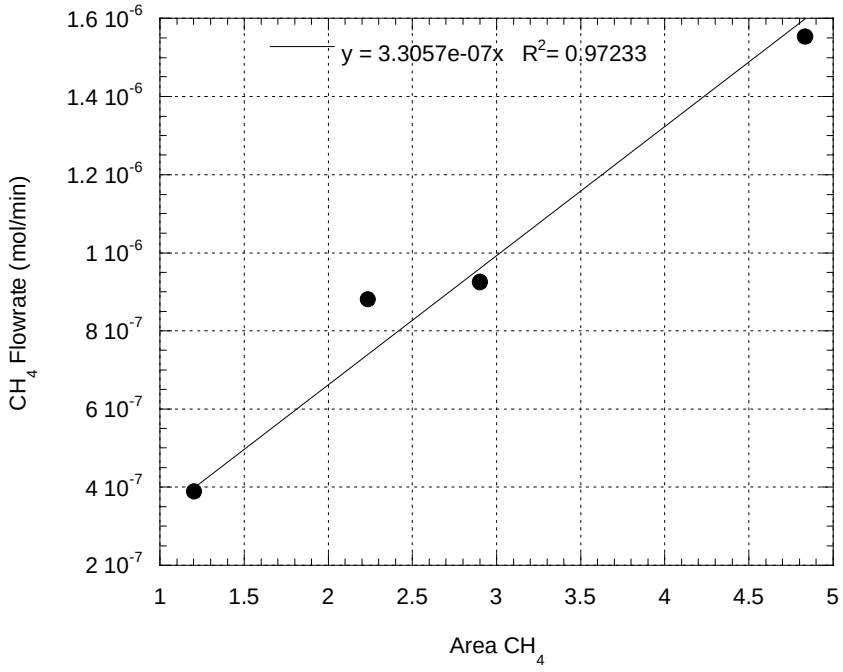

Figure A.11. *Effect of temperature on quantification of methane via an IS*[14]

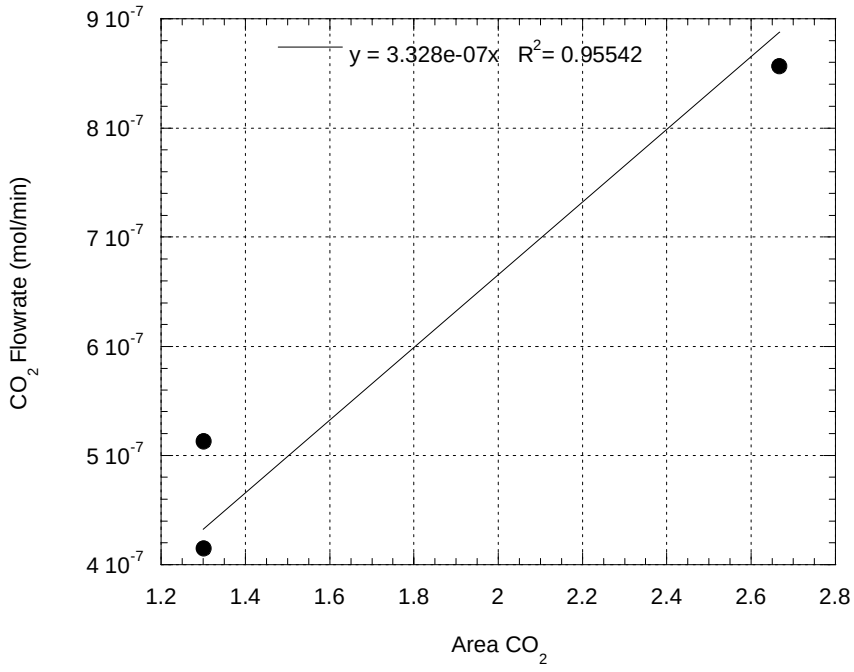

Figure A.12. *Effect of temperature on quantification of CO_2 via an IS*[14]

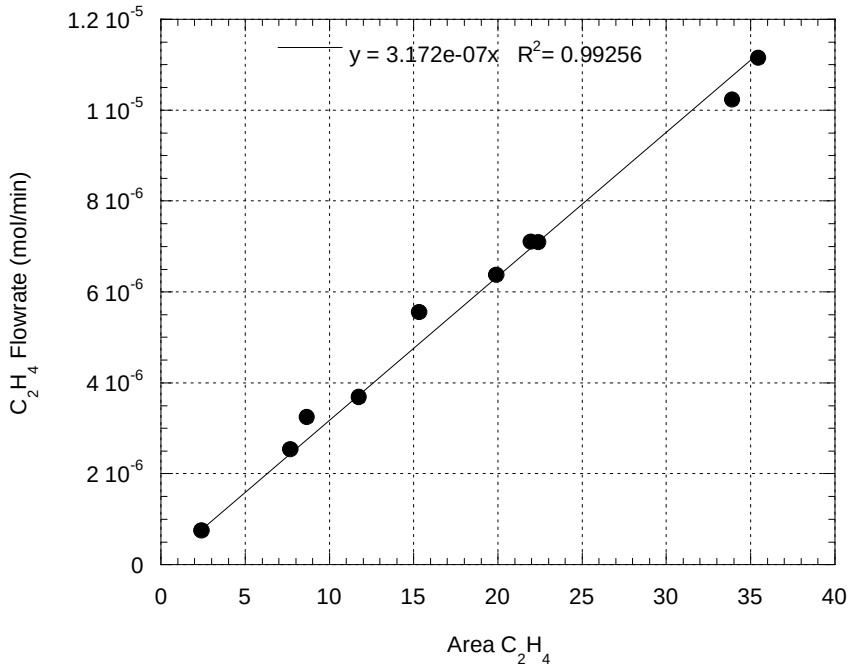

Figure A.13. *Effect of temperature on quantification of ethylene via an IS*[14]

APPENDIX F

SAMPLE EXPERIMENTAL PROCEDURE

Table A.7. *Sample experimental procedure*

Reactor Temperature (°C)	**GC Analysis**	**Duration (min)**	**Time** 8:30
200 (No liquid feed)	Steady state in GC	120	10:30
200 (No liquid feed)	Ar calibration	40	11:10
200	Ar calibration	15	11:25
200	C_2H_4O calibration	55	12:20
200	C_2H_6O-H_2O calibration	60	13:20
200	C_2H_4O calibration	55	14:15
200	Effluent for 200°C	60	15:15
200	Effluent for 200°C	60	16:15
300	Effluent for 200°C	60	17:15
300	H_2 calibration	60	18:15
300	Effluent for 300°C	60	19:15
300	Effluent for 300°C	60	20:15
350	Effluent for 300°C	60	21:15
350	C_2H_6O-H_2O calibration	60	22:15
350	Effluent for 350°C	60	23:15
350	Effluent for 350°C	60	0:15
400	Effluent for 350°C	60	1:15
400	Effluent for 400°C	60	2:15
400	Effluent for 400°C	60	3:15
450	Effluent for 400°C	60	4:15
450	Effluent for 450°C	60	5:15
450	Effluent for 450°C	60	6:15
500	Effluent for 450°C	60	7:15
500	Effluent for 500°C	60	8:15
500	Effluent for 500°C	60	9:15
Shutting down	Effluent for 500°C	60	10:15
Shutting down	Calibration gas	55	11:10
Shutting down	Shutting down	60	12:10
Total Time		1660 min (27.7 h)	

APPENDIX G

SETUP PICTURES

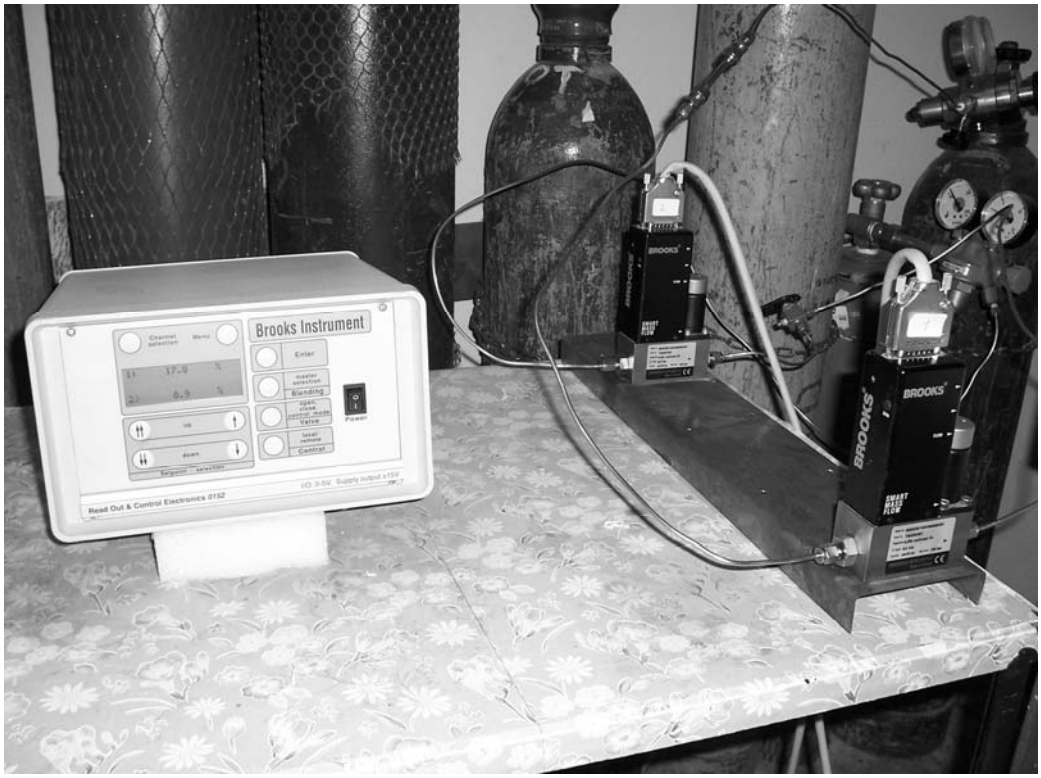

Figure A.14. *Gas cylinders and mass flow controllers*

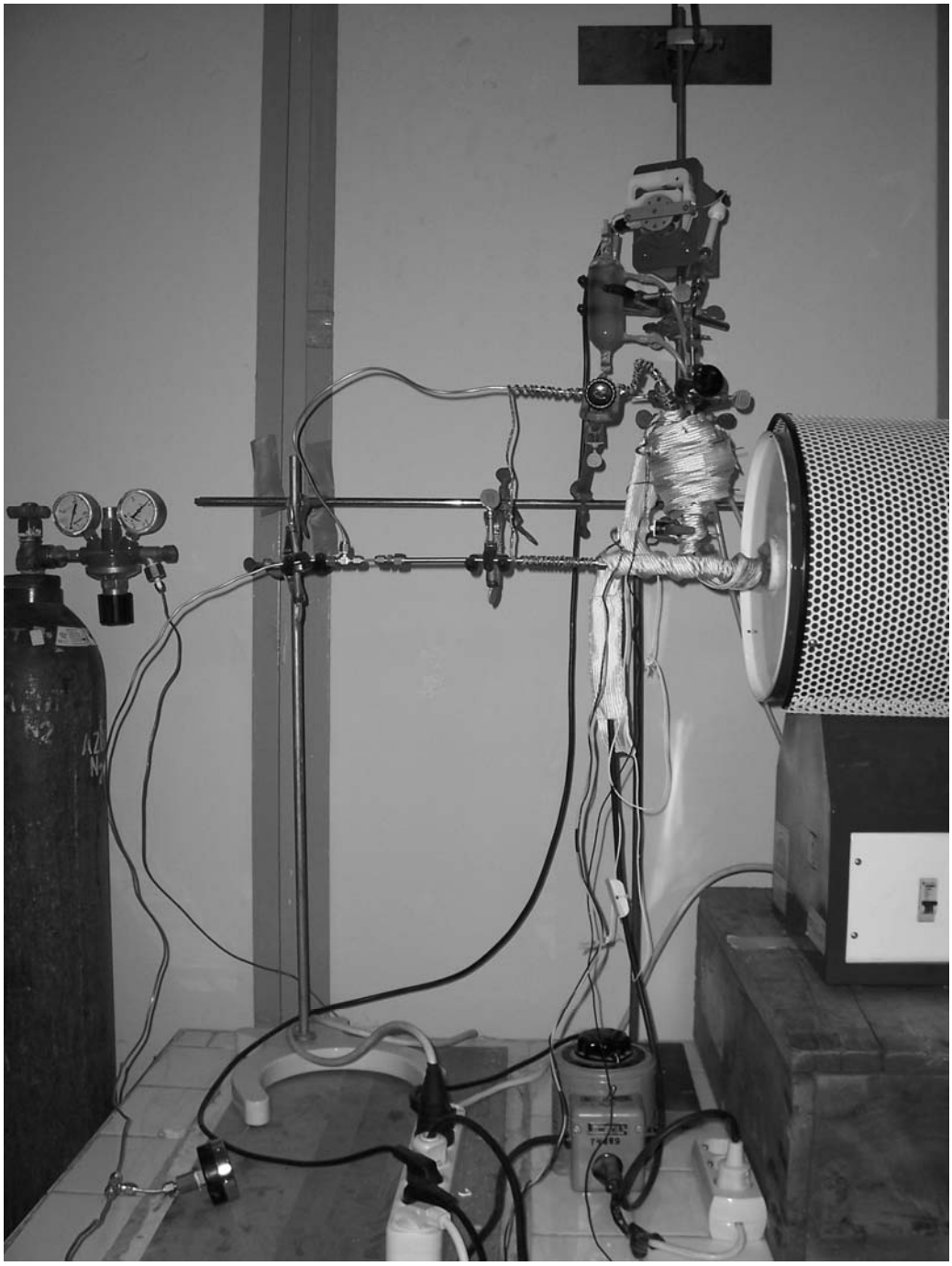

Figure A.15. *Feeding unit*

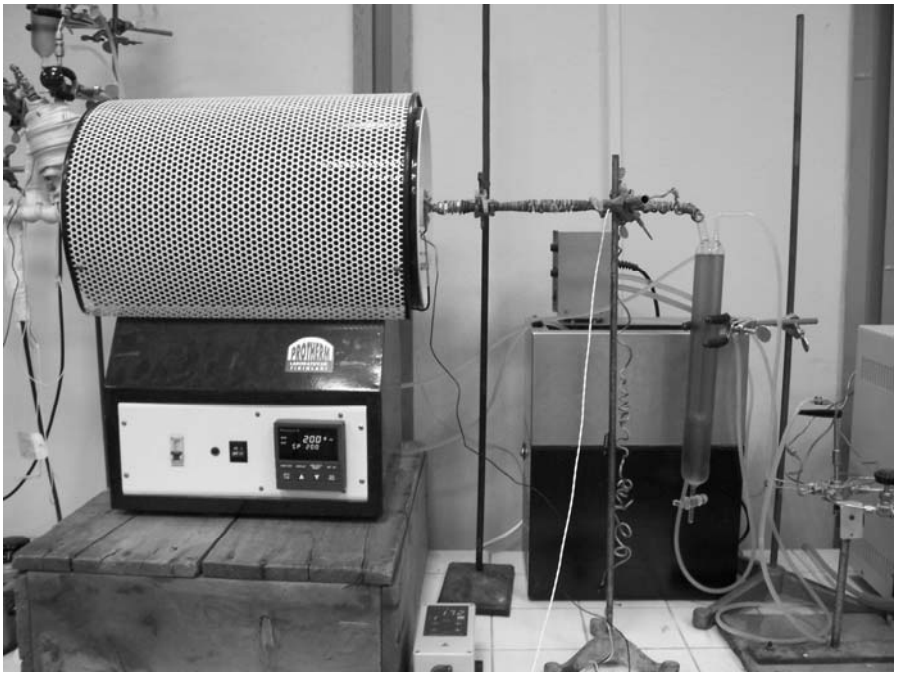

Figure A.16. *Reacting unit*

Figure A.17. *Analyzing unit (GC)*

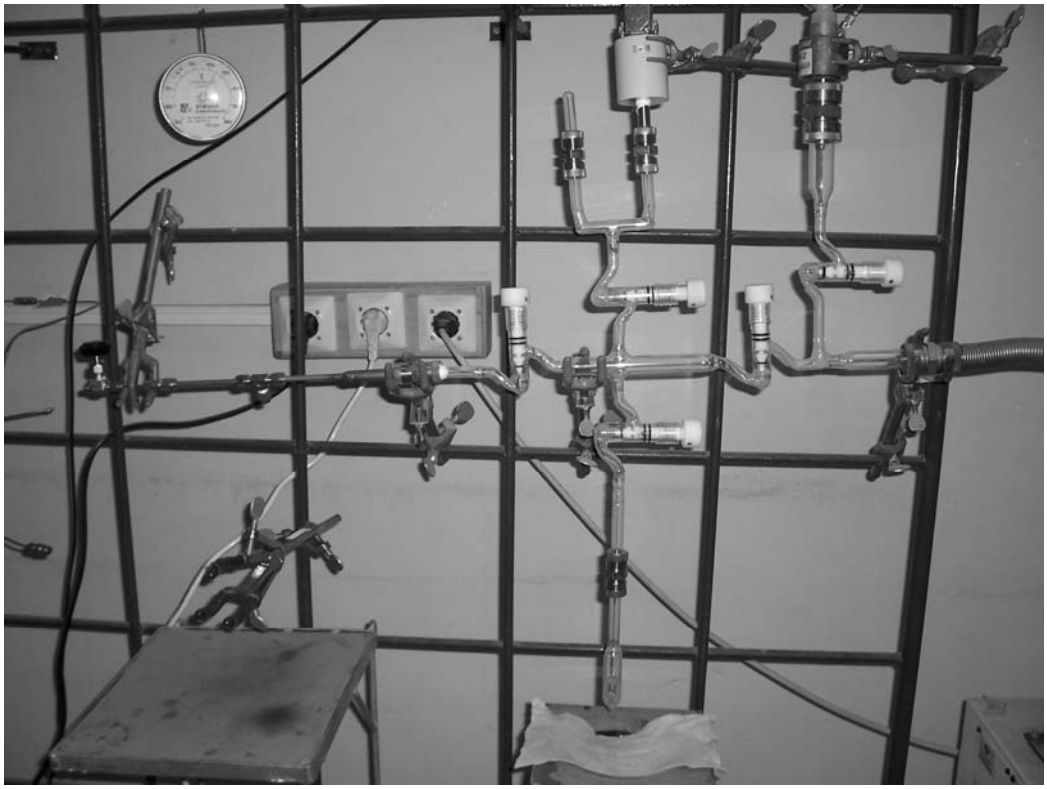

Figure A.18. *Manifold used in gas calibrations*

TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

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OBJECTIVE

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor development work. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Studies will be conducted to define the chemical phases present at various stages of the activation and synthesis and to define changes that occur during these stages. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

SUMMARY OF RESULTS

A. CATALYST ACTIVATION

A.1. Activation with Hydrogen. Hydrogen reduction results in the reduction of Fe_2O_3 to Fe_3O_4 and then to metallic Fe. Metallic iron has a propensity to sinter so that catalysts prepared by this technique have low surface areas if temperatures in the range of 400°C are employed.

A.2. Activation with CO. An easy and reproducible procedure for catalyst activation involves treating the iron catalyst with CO at 270°C during a 24 hour period. In this reaction, the reduction of iron is effected by the production of CO_2. At the same time, the carbide may be formed using the carbon deposited by the Boudourd Reaction.

Based upon the rate of formation of CO_2, the reduction leads to the formation of Fe_2O_3 to Fe_3O_4 and then to a mixture of iron carbides. This procedure produces carbon during a 24 hour period

that is in excess of that needed to form iron carbide. This method is especially attractive since the presence of traces of sulfur in the catalyst does not result in the formation of H_2S which is a severe catalyst poison. The CAER has obtained very similar curves of the extent of reduction/carbide formation versus time for conversion in 1-liter CSTRs and in a 2"x6' bubble column reactor; the CAER data was subsequently confirmed by an activation run with approximately 1,000 pounds of catalyst in the DOE LaPorte pilot plant. The disadvantage of this procedure is that in a typical syngas plant there is not a stream of pure CO. Furthermore, whereas hydrogen can be obtained in high purity from a syngas stream using membrane diffusion processes, it is not possible to easily separate pure CO from a syngas stream.

A.3. Activation with Syngas. There are conflicting reports of the success in activating a catalyst in syngas at medium or high pressure reaction conditions. When success has been reported, the catalyst was usually contacted with lower temperatures and low flow rates and then the temperature was gradually elevated to the desired reaction temperature. In work at the U.S. Bureau of Mines in the late 1940s-early 1950s, they would adjust the flow of syngas to maintain about 20 vol.% CO_2 in the exit gas. In some cases, it would require several days until the maximum conversion was obtained with this activation procedure. For activation at reaction pressure, we find that there is nearly a linear relationship between the mole fraction of hydrogen in the activation gas and the conversion of CO; i.e., the higher the fraction of hydrogen in the synthesis gas the lower the CO conversion. Even after 24 hours of activation in synthesis gas with a low mole fraction of hydrogen, the conversion may increase during a three to five day period. It appears that the ultimate activity of the iron catalyst is directly related to the partial pressure of hydrogen and that the activity declines as the hydrogen partial pressure increases. On the other hand, if activation with syngas is effected at atmospheric pressure, the presence of hydrogen does not appear to have an impact so that comparable activities can be obtained for activations conducted with only CO or with syngas.

A.4. Role of Copper. Copper may be an important component of an iron catalyst. The copper provides a very beneficial effect if the catalyst is to be reduced in hydrogen during the activation procedure. Since the addition of copper allows the reduction to be effected at a lower temperature, the resulting surface area following reduction of an iron catalyst containing copper is higher than one which does not contain copper. Even when the reduction/carbiding is conducted with CO, it appears that the copper allows these operations to be conducted at a slightly lower temperature. It appears that the presence of copper (in the 1-4 wt% range) does not alter the product selectivity from that of a catalyst with the same composition without copper.

B. CATALYST AGING

One of the targets for the CAER work was to prepare a catalyst that would have an initial CO conversion of 90% and a decline in CO conversion that was less than 1% per week of operation. These two targets were to be met using reaction conditions that were identical to those utilized

by Kölbel and coworkers in the German work using slurry reactors (1) except that the flow rate of the reactant gases was to be 50% greater than the German worker utilized. It has been shown that the CAER produced catalysts attained the initial CO conversion and the slow deactivation rate during up to about 4,000 hours (166 days; 5.5 months) of continuous operation. Several tests have been conducted for 2,000 hours or longer and each attained a catalyst deactivation rate of 1% CO conversion/week or less.

Catalyst aging data have been obtained for a pure iron catalyst and three catalysts containing promoters. It is evident that all four catalysts had a similar high activity during the initial 200 hours of testing. Only after this period did differences in aging become apparent. The iron catalyst containing potassium aged more rapidly than the one that contained only iron. On the other hand, the addition of silicon to the iron catalyst caused the aging to occur at a slightly slower rate than for the pure iron catalyst. There is a strong synergism between iron, potassium and silicon since this combination produces a catalyst with outstanding long-term stability.

Various reasons have been offered to account for the gradual loss in activity of the catalysts. However, we have been unable to identify a single factor that could account for the different catalyst aging treads for the four catalysts. For example, water vapor provides an oxidizing atmosphere; however, the partial pressure of water vapor in contact with the catalyst cannot account for the different aging rates. Likewise, carbon deposition, as measured by total carbon content, cannot account for the difference in the aging rates. Loss of surface area cannot account for the aging rate differences since all catalyst's surface areas **increase** with time on stream, most likely due to the deposition of carbon. This data indicates that it is necessary to conduct reasonably long-term testing of the catalyst if significant differences in stability are to be elucidated.

C. CATALYSTS CHARACTERIZATION - TRENDS WITH TIME

While the composition of the catalyst following activation depends upon the activation procedure, in general the catalyst will contain a significant fraction of iron carbide. Activation in pure CO or in a syngas mixture at atmospheric pressure produces the highest fraction of iron carbides following 24 hours of activation. However, during the course of the synthesis, the composition of the catalyst gradually changes to produce a higher fraction of Fe_3O_4. Thus, the iron catalyst undergoes significant phase and chemical composition changes during use for synthesis.

The characterization has been conducted using X-ray diffraction, Mössbauer spectroscopy, surface area, elemental analysis, scanning electron microscopy and transmission electron microscopy, including high resolution transmission electron microscopy. In general, we have not found the changes in activity to be directly related to the phase or chemical composition of the catalyst.

D. PRODUCT SELECTIVITY

Both types of promoters impact selectivity although the alkali promoter has a greater impact than the structural promoter (silica or alumina). It appears that alumina impacts the product selectivity by the production of **more oxygenates** and a **higher alkene content of the higher carbon number hydrocarbons**. The production of more oxygenates (essentially an equilibrium value of the primary alcohol and corresponding aldehyde or the secondary alcohol and the corresponding ketone) with the alumina promoter is surprising since free aluminium oxide is a far better alcohol dehydration catalyst than silica. At least in the fresh, oxide catalyst form, both aluminium and silicon are substituted into the Fe_2O_3 as judged by the shifts of the iron oxide X-ray diffraction peak positions. This result implies that the Al and Si are not present as the metal oxide even in the carbided catalyst.

The potassium (and other alkalis to a smaller extent) affect both the molecular weight distribution of the products (and indirectly the methane production) and the amount of alkenes in each carbon number fraction. In general, a higher potassium content produces higher weight products. Thus, whereas the value of alpha (the ratio of chain propagation to chain termination) is about 0.7 for unpromoted iron or a catalyst containing up to about 0.5 wt.% potassium, the value of alpha can be increased to greater than 0.9 with catalysts containing higher amounts of potassium.

For conversions at 270°C, the ethene/(ethane + ethene) ratio is very dependent upon the potassium content, ranging from about 0.3 for no potassium to about 0.7 for potassium 0.1 K/Fe. For the C_3 and C_4 fraction, the alkene will account for 80% or greater of the product for as little as 0.07 K/Fe. For the C_5-C_{12} fraction, 65% or greater of the hydrocarbon products are alkenes for 0.07K/Fe. The fraction of alkenes decrease with increasing carbon number and the rapidity of the decline depends upon the alkali level in the catalyst. The alpha-olefin content of the C_4-fraction is usually 0.8 or higher, and decreases with increasing CO conversion and carbon number fraction. In general, decreasing the reaction temperature and the CO conversion level leads to a higher alkene content and a higher alpha-olefin content.

E. CONVERSIONS IN 1-LITER CSTR AND 2"X6' BUBBLE COLUMN REACTOR

CAER personnel have made several runs in the 2"x6' slurry bubble column reactor (SBCR). The four initial runs were to activate an iron catalyst to be utilized in the DOE LaPorte, Texas pilot plant. The activation was conducted in CO and the four runs were conducted to obtain activated catalysts for filtration testing under the supervision of Air Products personnel. The catalyst had been spray dried to produce spherical particles in the 30-40 micron range. The four runs produced reproducible activation data with respect to the rate and extent of catalyst activation. The runs in the SBCR produced data that were in excellent agreement with runs at the CAER in CSTRs and at the LaPorte pilot plant run.

F. PROCESS CONSIDERATIONS BASED ON CATALYST ACTIVITY/SELECTIVITY

Based upon the selectivity changes for the relative conversion of H_2 and CO, the catalyst productivity as a function of CO conversion, and the relative contribution of WGS and hydrocarbon production, a process based upon a series of smaller reactors rather than one large reactor or a process with low conversion and gas recycle is preferred.

The general feeling is that the FTS should be carried out at high syngas conversion. During the past 50 years significant increases have been made in developing catalysts with high activity. A comparison, based on assigning work at the Bureau of Mines using fused iron catalysts, is given in the following table.

		Relative Activity
1950	U.S. Bureau of Mines	1
1955	Kölbel	15
1980s	Mobil	13
1993	CAER	21
1996	CAER	43

Thus, there has been about a thirty fold increase in syngas conversion at high total conversion levels during the fifty years. However, there is a rapid increase in conversion with increasing contact time up to about 60% CO conversion levels; however, the increase in conversion becomes much slower above this 60% level. For example, it is possible to obtain a significantly higher hydrocarbon productivity per unit of catalyst by operating at a lower conversion level. At the higher conversion level (90% CO conversion), about 0.5 grams of hydrocarbon/g Fe/hr. are produced; however, at a conversion of 40% for CO, the hydrocarbon productivity becomes about 3 grams/g. Fe/hr. In addition, much less carbon is converted to CO_2 and the products contain a significantly higher content of alkenes.

Thus, based only on catalyst considerations, it is highly desirable to utilize several reactors in series. One scenario to do this would involve the use of smaller reactor sizes in the subsequent reactors. Another, and the preferred, method is to utilize the same size reactors. However, it should be noted that there is a conversion level where the composition of the exit gas is the same as the feed stream, a point that we refer to as the equivalence point. Thus, when the same size reactors are utilized, water would be removed between the reactors and makeup syngas would be added to make up for that which has been converted. Thus, all reactors would operate under identical conditions but the overall effect is to attain an equivalent high conversion using smaller, more productive reactors.

Another major problem is whether one should operate using a low or high alpha catalyst to produce transportation fuels. At Sasol, both options are utilized. The high temperature fluidized bed reactors produce products that are equivalent to a low alpha catalyst whereas the Arge and slurry reactors operate to produce high alpha products. Shell operates to produce high alpha products. When the high alpha catalyst is utilized, transportation fuels are produced from the high molecular weight products by hydrocracking. However, a plant that will emphasize transportation fuels must also convert the low molecular weight products to transportation fuels (3). The Mossgas operation in South Africa currently utilizes a Süde Chemie zeolite oligomerization catalyst to convert light olefins to transportation fuels. They report that the catalyst can be operated without separating the water and oxygenates from the alkene-rich stream.

It appears that the oligomerization route has appeal since this would permit one to operate with a low-alpha iron catalyst that would not produce a significant quantity of high molecular weight products. Thus, it would be possible to operate the slurry reactor without having to carry out catalyst/wax separation within the reactor in order to maintain an adequate inventory of catalyst in the reactor.

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