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Bifunctional catalyst for direct DME synthesis

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BIFUNCTIONAL CATALYST FOR THE DIRECT DME SYNTHESIS

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MASTER THESIS

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ABSTRACT

New technologies produce liquids from synthesis gas in the gas to liquids technology (GTL). Dimethyl ether made from synthesis gas is one such possible process. DME is more or less claimed to be a renewable fuel that solves the issues concerning CO_2 emissions and global warming. Nowadays, DME is commercially produced by dehydration of methanol using acidic porous catalysts; whereas direct synthesis from synthesis gas in large-scale plants might be more economical. A collection of bifunctional catalysts with different contents and additives has been studied for the direct DME synthesis. In the current study, a sample of $CuO–ZnO–Al_2O_3$ was prepared by co-precipitation method. After characterization by XRD, the catalyst was mixed with methanol dehydration catalyst (HZSM-5) with different mass ratios(1,2,4,6 and 8). The activity test for the catalysts was performed in the DME synthesis set-up. The experiment was carried out in a fixed-bed reactor and the temperature range of 235-275°C , the GHSV range of 4500 - 60000 nmL/(g_{cat}.h) and H_2:CO ratios of 1,2 and 4 were applied.

According to the results; The bifunctional catalyst with mass ratio of 6 shows the better performance for different GHSVs. The relatively large surface area of the HZSM-5 catalyst provides proper utilization of methanol produced by methanol synthesis catalyst for the ratios up to 6. The bifunctional catalysts with mass ratios of 4, 6 and 8 show the same DME yields at temperature range of 235-255°C. At the higher temperatures, the bifunctional catalysts with mass ratios of 4 and 6 show higher CO conversions and DME yields. H_2-rich feeds give better CO conversion and DME yield. The bifunctional catalyst with mass ratio of 6 shows higher CO conversion and by increasing the mass ratio, there will be no increase in CO conversion. **According to the results the optimum $CuO-ZnO-Al_2O_3$ to HZSM-5 mass ratio could be between 4-6.**

I declare that this is an independent work according to the exam regulations

of the Norwegian University of Science and Technology

Date and signature: 29 June 2011 Ayob esmaelpour

LIST OF FIGURES

LIST OF TABLES

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ABSTRACT

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NOMENCLATURE

Symbol	Unit	Description
ΔH_{298}	kJ/mol	Standard enthalpy change of reaction
K_i	-	Adsorption equilibrium constant for component i
K_n	-	chemical reaction constant
$K_{P,n}$	-	Equilibrium constant for reaction n
k	$kgmol/m^3 \cdot h$	Rate constant
k_0	$kgmol/m^3 \cdot h.kpa$	Rate constant
N	m^3/h	Flow rate
n_i	mole	The moles of component i
P	bar	Pressure
P_i	atm	The partial pressure of component i
Q	nml/min	Volumetric flow
Q_i	nml/min	Volumetric flow of component i
S_i		Selectivity to component i
T	°C	Temperature
X_i		The conversion of component i
W	gr	Weight
Y_i		The yield of component i
α		Fraction of Cu-based catalyst in the catalyst mixture

1 INTRODUCTION

According to the International Energy Outlook 2010, world energy consumption is expected to grow 49 percent from 2007 to 2035 (1). Oil powers cars, trucks, boats, ships, airplanes, etc. The rise in crude oil prices and fast decrease of oil reserves have cause an increase in demand for substitute energy sources such as natural gas, coal and biomass.

On the other hand, the fossil fuels are harmful to the environment and the major companies have seen the possibilities and advantages of more environmentally benign fuels. Recent energy legislation promotes research on capturing and storing greenhouse gas emissions and improving vehicle fuel efficiency, among other goals.

New technologies produce liquids from *synthesis gas*[1] in the gas to liquids technology (GTL). The GTL process is capable of producing products that could be blended into refinery stock as superior product with fewer pollutants. In addition, in the case of natural gas, the transportation and distribution of liquids, synthesized from natural gas, are cheaper than that for natural gas to the large markets.

Catalytic conversion of synthesis gas to more useful chemicals and fuels is a challenge for the 21st century (2). Dimethyl ether made from synthesis gas is one such possible process. DME is more or less claimed to be a renewable fuel that solves the issues concerning CO_2 emissions and global warming. This is, however, as dependent of the source of the syngas (natural gas/coal/biomass) as for any other product of synthesis gas (Fischer-Tropsch diesel, methanol, ammonia, hydrogen). In all cases, the use of biomass for syngas generation is challenging in terms of cost and efficiency, whereas natural gas is favoured from this point.

Dimethyl ether (DME) is the simplest ether having the chemical formula: CH_3OCH_3. DME is a colourless and chemically stable gas. It is a volatile organic compound, but is non-carcinogenic, non-teratogenic, non-mutagenic and non-toxic. DME burns with a visible blue flame (3). It has a boiling point of - 25.1°C and a vapour pressure of about 5.3 bars at ambient temperature, which makes DME easily liquefied. The physical properties of DME are very similar to those of LPG[2], thus DME can be distributed and stored using LPG handling

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[1] Synthesis gas or Syngas is the name given to a gas mixture that contains varying amounts of carbon monoxide and hydrogen.

[2] Liquefied petroleum gas

technology. Table 1.1 shows properties and combustion characteristics of DME and diesel fuel. Traditionally, DME has been used to produce intermediate chemicals such as dimethyl sulfate or oxygenated compounds (4). The beneficial properties of using DME as a substitute for LPG and LNG[1] in power plants, and as a diesel substitute in vehicles makes DME a good candidate for high-quality fuel for the next generation.

Table 1-1: Properties of DME and diesel fuel (5).

Properties	DME	Diesel fuel
Molar mass(g/mol)	46	170
Liquid density(kg/m^3)	667	831
Cetane number	>55	40-50
Auto-ignition temperature(K)	508	523
Boiling point at 1 atm(K)	248.1	450-643
Enthalpy of vapourization(kJ/kg)	467.13	300
Lower heating value(MJ/kg)	27.6	42.5
Kinematic viscosity of liquid (cSt)	<0.1	3
Surface tension (at 298 K) (N/m)	0.012	0.027
Vapour pressure (at 298 K) (kPa)	530	<<10

It is a clean fuel of high cetane number with excellent combustion characteristics. The diesel engines need only small changes to run on liquid DME. However the concept might need more time to grow. NO_x emissions from DME-fuelled engines can meet future regulations (6). The substance does not contain sulphur or ash. The combustion of DME has lower CO_2-emission and as DME does not contain sulfur or ash, generates no SO_x or particulate matter (7). Therefore it has more environmentally attractive properties compare to the existing fuels. As petrochemical feedstock DME has potential. One example is the production of olefin from DME.

Synthesis gas and methanol are the main feedstocks for DME synthesis. **Synthesis gas** or syngas refers mostly to mixtures of hydrogen and carbon monoxide. It may contain carbon dioxide together with some nitrogen and other inert gases, depending from the production process and the application.[2] Synthesis gas can be produced from almost any carbon source ranging from natural gas and oil products to coal and biomass via reforming or gasification processes. The most important applications of syngas are in methanol synthesis, the hydroformylation of alkenes to aldehydes and alcohols, and the synthesis of larger hydrocarbons (Fischer–Tropsch) (8).

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[1] Liquefied natural gas

[2] The mixture of nitrogen and hydrogen used for the synthesis of ammonia is also called synthesis gas.

1 INTRODUCTION

Methanol is the simplest alcohol and is a colorless, polar and flammable liquid. Traditionally, methanol is produced from natural gas today. The other feedstocks such as municipal waste, biomass, agricultural products can be used for methanol production. Methanol is used as a feedstock for many chemicals and products. A relatively large amount of methanol is converted to formaldehyde, and from there into products such as plywood, paints and explosives. Methanol as a chemical feedstock, a fuel, or a fuel additive covers most present methanol consumption. Other uses of methanol can be classified into four areas: solvent, antifreeze, inhibitor and substrate (9).

There are many technically challenging opportunities for the improvement of the existing processes or development of modern processes for the present use of methanol and in developing new uses. For the case of current study, it is well known that DME can be produced from methanol dehydration over acid catalysts under relatively mild conditions (9).

2 THEORIES

2.1 DME synthesis processes

Until the late 1970s DME was produced as a by-product of the high temperature methanol technology, based on a co-production of methanol and DME (10). Nowadays, DME is commercially produced by dehydration of methanol using acidic porous catalysts such as zeolites, silica–alumina, alumina, etc (11); whereas direct synthesis from synthesis gas in large-scale plants might be more economical (10). In the indirect process synthesis gas is first converted to methanol and then further to DME. In the direct synthesis process, both the methanol formation reaction and the methanol dehydration reaction take place in the same reactor over a bifunctional catalyst.

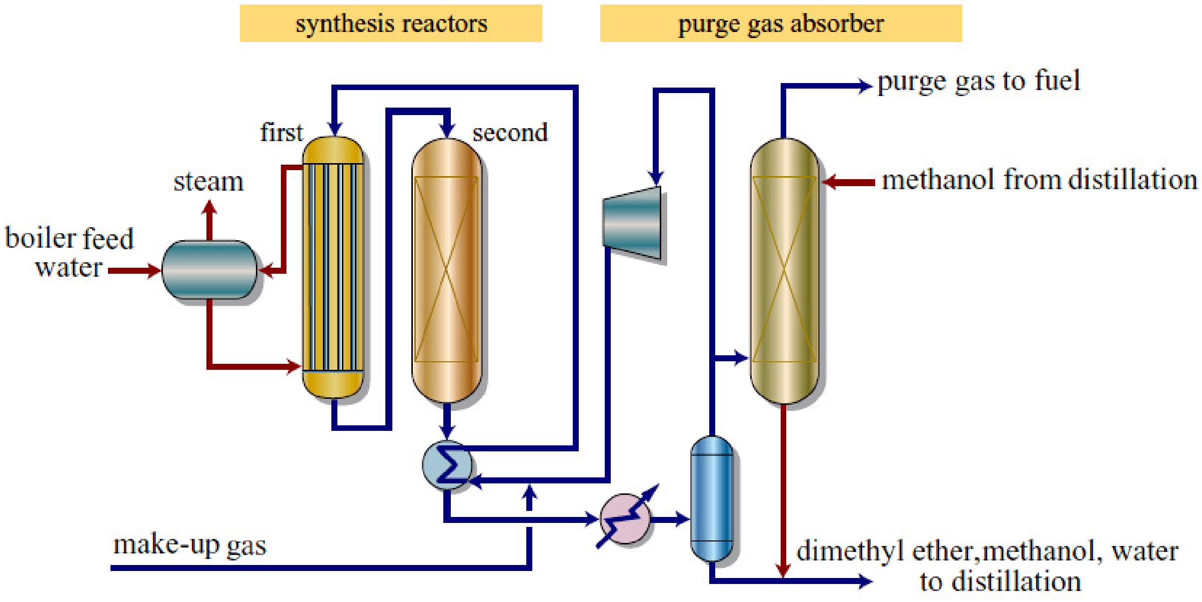


Figure 2-1: Combined synthesis of methanol and DME. Simplified process flow diagram (12).

2.1.1 DME synthesis from Synthesis Gas

2.1.1.1 Synthesis Gas production

Steam methane reforming (SMR) is the predominant commercial technology for syngas production, in which methane and steam are catalytically converted to hydrogen and carbon monoxide. Partial oxidation is a non-catalytic reaction of methane and oxygen to produce a syngas mixture. SMR and partial oxidation produce syngas with appreciably different compositions and particularly, SMR produces a syngas having a much higher H_2:CO ratio (8). The main technologies for synthesis gas production from natural gas are summarized and compared on Table 2-1.

Table 2-1: Comparison of syngas production technologies from natural gas (8).

Technology	Advantages	disadvantages
SMR	• Most extensive industrial experience • Oxygen not required • Lowest process temperature requirement • Best H_2:CO ratio for hydrogen production applications	• H_2:CO ratio often higher than required when CO also is to be produced • Highest air emissions
Heat exchange reforming	• Compact overall size and "footprint " • Application flexibility offers additional options for providing incremental capacity	• Limited commercial experience • In some configurations, must be used in tandem with another syngas generation technology
Two-step reforming	• Size of SMR is reduced • Low methane slip favors high purity syngas applications • Syngas methane content can be tailored by adjusting secondary reformer outlet temperature	• Increased process complexity • Usually requires oxygen • Higher process temperature than SMR
ATR	• Natural H_2:CO ratio often is favorable • Lower process temperature requirement than POX • Low methane slip • Syngas methane content can be tailored by adjusting reformer outlet temperature	• Limited commercial experience • Usually requires oxygen
POX	• Feedstock desulfurization not required. • Absence of catalyst permits carbon formation and therefore, operation without steam, significantly lowering syngas CO content • Low methane slip • Low natural H_2:CO ratio is an advantage for applications requiring ratio < 2.0	• Low natural H_2:CO ratio is a disadvantage for applications requiring ratio > 2.0 • Very high process operating temperatures • Syngas methane content is inherently low and not easily modified to meet downstream processing requirements • Usually requires oxygen • High temperature heat recovery and soot formation/handling adds process complexity

The required properties of the syngas are different for the different uses. In general, synthesis gas ideally has the same stoichiometry as the final product. The synthesis gas composition for several processes is shown in Table 2-2.

The syngas composition can be manipulated by different process conditions and/or by using additional process steps. Table 2-3 shows the main techniques for adjusting the syngas H_2:CO ratios.

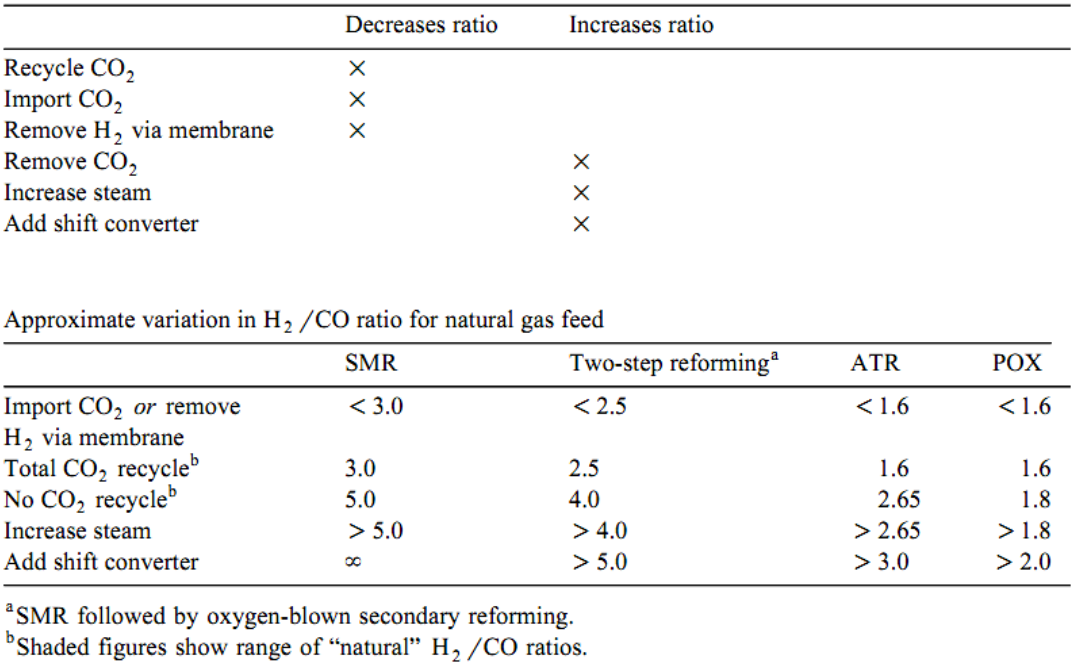
Table 2-2: Syngas composition for various processes (10; 13).

Process[Product]	Syngas composition	Add. feedstock
DME	$\frac{H_2}{CO} \approx 1-2$	
Methanol ,High temperature Fischer-Tropsch [Gasoline via TIGAS [a]]	$M = \frac{H_2 - CO_2}{CO - CO_2} \approx 2$	
Low temperature Fischer-Tropsch	$\frac{H_2}{CO} \approx 2$	
Carbonylation [acetic acid]	CO	Methanol
Hydroformulation [higher alcohols]	$\frac{H_2}{CO} \approx 1$	Olefins
[Industrial hydrogen for refineries]	99.99 H_2	
[Hydrogen for PEMFC[b]]	< 50 ppm CO	
Reducing gas [Iron ore]	$\frac{H_2O + CO_2}{H_2 + CO + CO_2 + H_2O} \leq 0.05$	

[a] Topsoe integrated methanol/DME and gasoline synthesis

[b] Polymer electrolyte fuel cell

Table 2-3: Techniques for adjusting the syngas H2:CO ratios (8).



	Decreases ratio	Increases ratio
Recycle CO_2	×	
Import CO_2	×	
Remove H_2 via membrane	×	
Remove CO_2		×
Increase steam		×
Add shift converter		×

Approximate variation in H_2/CO ratio for natural gas feed

	SMR	Two-step reforming[a]	ATR	POX
Import CO_2 *or* remove H_2 via membrane	< 3.0	< 2.5	< 1.6	< 1.6
Total CO_2 recycle[b]	3.0	2.5	1.6	1.6
No CO_2 recycle[b]	5.0	4.0	2.65	1.8
Increase steam	> 5.0	> 4.0	> 2.65	> 1.8
Add shift converter	∞	> 5.0	> 3.0	> 2.0

[a] SMR followed by oxygen-blown secondary reforming.

[b] Shaded figures show range of “natural” H_2/CO ratios.

2.1.1.2 DME synthesis from Synthesis Gas: reactions

The direct process produces DME directly from synthesis gas. This process features a bifunctional[1] catalyst with activity for both the synthesis of methanol and the synthesis of DME.

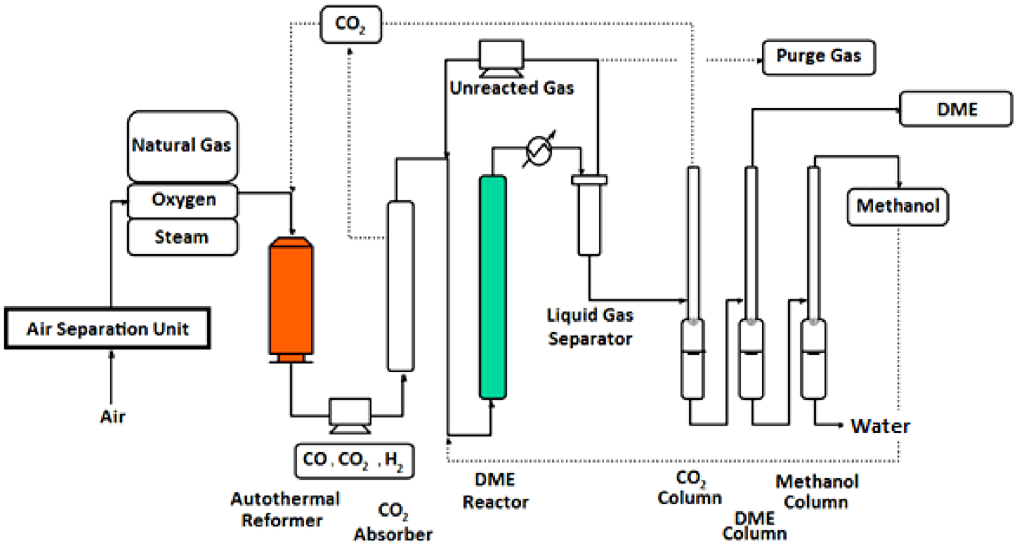


Figure 2-2: Direct Production of DME (14).

For the direct method, four reactions take place in the syngas-to-DME reactor, namely (13):

Methanol synthesis reactions :	$CO + 2H_2 \leftrightarrow CH_3OH$	$\Delta H_{298} = -90.4$ kJ/mol	(2-1)
	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	$\Delta H_{298} = -49.4$ kJ/mol	(2-2)
Methanol dehydration :	$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$	$\Delta H_{298} = -23.0$ kJ/mol	(2-3)
Water gas shift (WGS) :	$CO + H_2O \leftrightarrow H_2 + CO_2$	$\Delta H_{298} = -41.0$ kJ/mol	(2-4)

The number of independent reactions for the direct DME synthesis is three. Since the reactions are reversible and exothermic, there is a need for excellent temperature control in order to maximize DME production. The reactions are thermodynamically favoured by low temperature. The methanol synthesis reactions, (2-1) and (2-2), are favoured by high pressures and they are more equilibrium-limited compare to the methanol dehydration reaction. When the dehydration reaction, reaction (2-3), takes place simultaneously, the syngas conversion increases. The reactor temperature and pressure range of about 220-290°C and 3-10 MPa and 260°C, 50bar as a standard

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[1] The catalyst mixture that contains both methanol synthesis and methanol dehydration catalysts.

condition have been reported (14; 13; 15). The main by-product of process is CO_2 and process requires a CO_2 capture unit.

The DME productivity and material utilization in a direct syngas-to-DME reactor is a strong function of the synthesis gas composition (13). F. Hayer et al. (13) studied the effect of H_2:CO ratio on the DME synthesis reaction. As Fig.2-4 shows the DME selectivity and productivity decrease with increasing the ratio. According to the results a H_2:CO ratio of 1 is optimum for DME selectivity but the ratio of 1–2 can be the optimum ratio for high productivity. However, high CO conversion can be obtained for the ratio of close to 2 or higher as long as DME synthesis equilibrium is not approached.

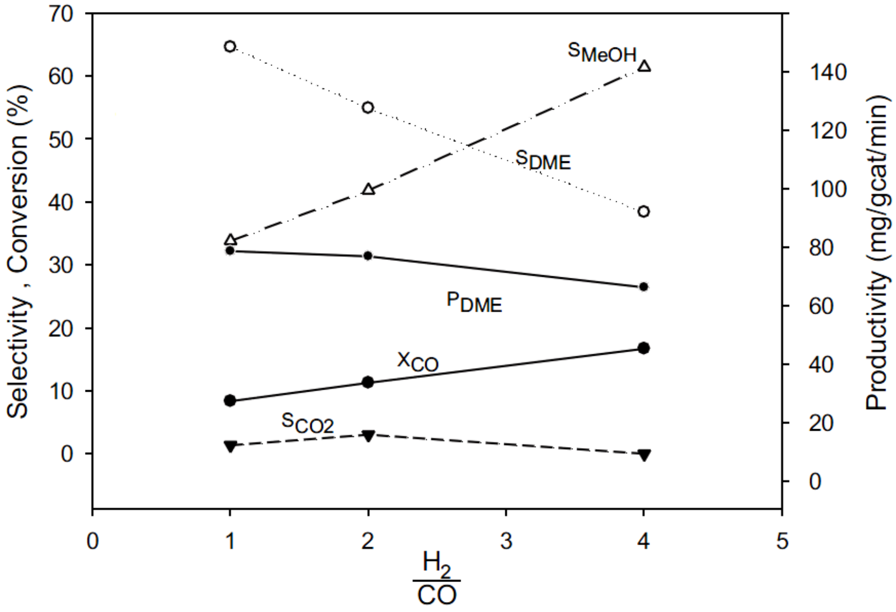

Figure 2-3: Effect of H_2:CO feed ratio on the DME synthesis reaction (13).

2.1.2 DME synthesis from Methanol

The indirect process, produces DME via the catalytic dehydration of methanol over an acidic catalyst (reaction 2-3). The reaction is mildly exothermic. This process has the advantages such as of enabling selection of the most optimum reactor type and operating conditions for each reaction steps. Due to less reaction heat compare to the direct process, reaction heat removal from the reactor is not a problem. Temperatures in the range 250-300°C and pressures up to 1.04 MPa have been reported (9). Various reaction mechanisms for methanol dehydration to DME have been reported. The proposed mechanism by S. J. Royaee et al. is described in appendix A.

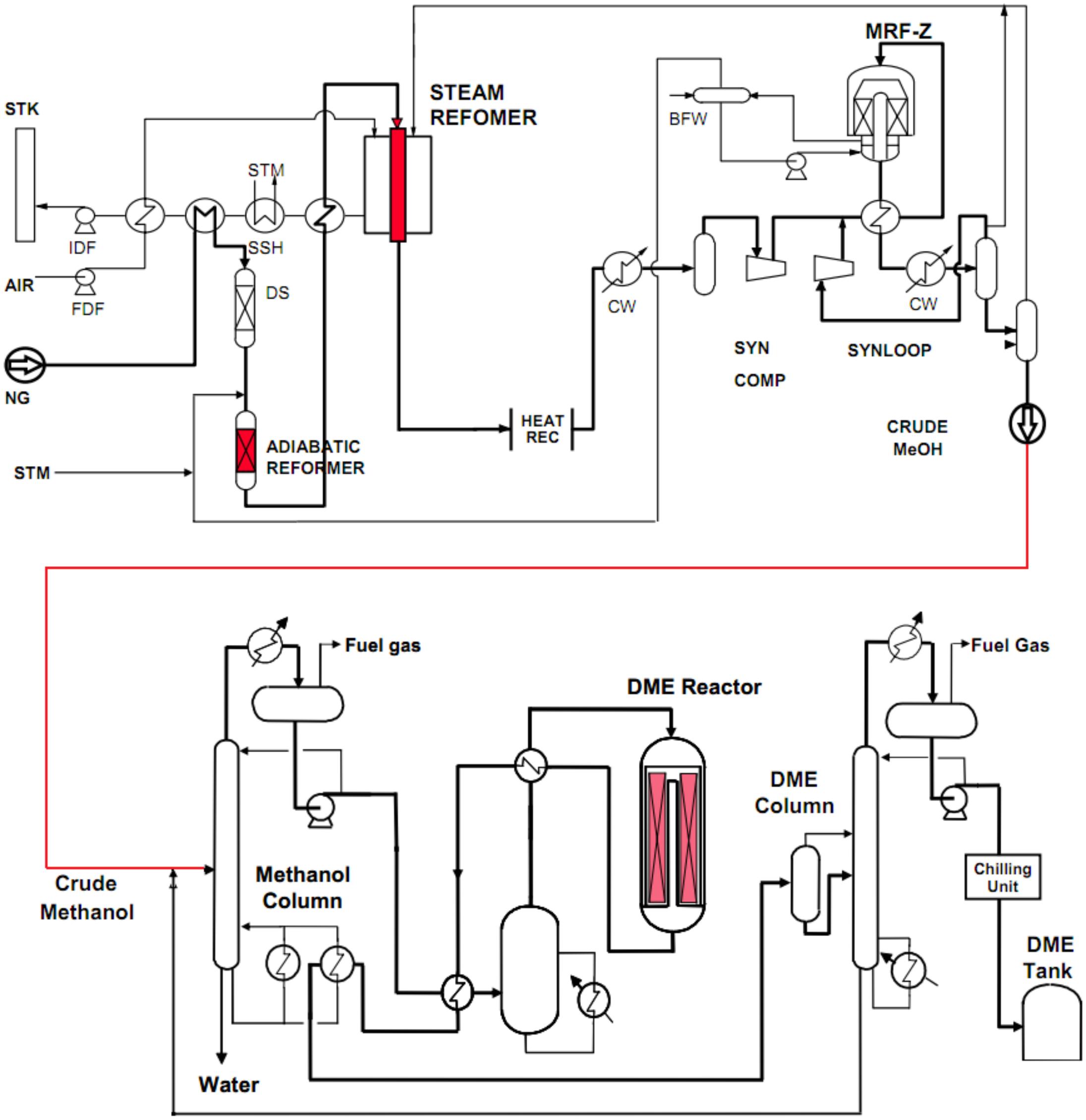

Figure 2-4: Indirect Production of DME (16).

2.1.3 Reactors for the DME synthesis processes

The main characteristics of DME synthesis process as a GTL process that must be considered in reactor design are (17):

- Highly exothermic reactions. The reactor must realize efficient and rapid removal of the accompanying large heat of reaction and provide a uniform temperature profile. Compare to methanol synthesis, the higher equilibrium conversion of DME synthesis could give more reaction heat and hot spot in the reactor can damage the catalyst (18).
- The process is operated at high temperature and pressure and the scale up must be easy. Developing a large scale production is critically important from the point view of the economy to produce low priced fuel.

The slurry bubble column, slurry airlift, fluidized-bed, fixed bed and microstructured reactors were used or studied for DME synthesis. The differences between these several reactor types are largely related to different approaches to temperature control and the choice of catalyst (17).

2.1.3.1 Slurry phase reactor

There are three types of slurry reactors: the bubble column, airlift reactor, and spherical reactor. The spherical reactor has economical feasibility and great potential for large scale production in the fuel industry, since it has higher mechanical resistance to pressure than the cylindrical column, which decreases the wall thickness needed and the reactor cost (17).

The advantages of the slurry reactors for GTL processes are: simple construction, good heat transfer performance, online catalyst addition and withdrawal, and reasonable interphase mass transfer rates with low energy input. However, as a multiphase reactor has some remarkable scale-up effects (17).

Due to the presence of an additional liquid phase, gas-liquid mass transfer limitations in a gas-liquid-solid slurry system may cause a decrease in the reaction conversion, especially at high solid concentrations and superficial gas velocities. In order to development and design of high-performance slurry reactors for GTL processes extensive studies are needed on the hydrodynamics, mass transfer, and liquid-solid separation(17).

Catalyst deactivation in slurry reactor may retard the development of these reactors. It has been reported that methanol synthesis and dehydration catalysts are stable when used separately in a slurry reactor. However, when physical mixture of these catalysts applied in LPDME[1] process, catalysts deactivate rapidly (19).

2.1.3.2 Fluidized-bed reactor

The fluidized bed reactor is proposed as an ideal reactor for the DME synthesis. Compared with the slurry reactor, the gas-solid mass transfer resistance is so small in a fluidized bed reactor that it can be neglected. On the other hand, the vigorous mixing of catalyst particles in the bed makes excellent temperature control achievable. Almost all of the reactions occur in the liquid phase, which contains the catalyst particles, whereas the gas phase does not contribute significantly to the reaction (19).

2.1.3.3 Fixed-bed reactor

Catalytic fixed-bed reactors are the most important type of reactor for the synthesis of large-scale basic chemicals and intermediates. In these reactors, the reaction takes place in the form of a heterogeneously catalyzed gas reaction on the surface of catalysts that are arranged as a so called fixed-bed in the reactor. In these reactors, poor temperature control and undesired thermal gradients may exist. Reactions with a large reaction heat as well as reactions with high temperature-sensitivity are carried out in these reactors with indirect heat exchange via a circulating heat transfer medium integrated in the fixed-bed (20; 21)

2.1.3.4 Microstructured reactors

A chemical reactor generally has to provide the necessary reaction time, introduce or remove the reaction heat and supply enough interface area between the phases in multiphase reaction systems. Microstructure reactors (MSR) possibly have these features (22). Chemical microstructured reactors (MSR) are devices containing open channels for fluids. The dimension of channels in MSR is about the sub-

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[1] Liquid Phase DME

millimeter range. Often MSR have multiple parallel channels with diameters between 10 and several hundred micrometers where the chemical transformation occur (23). High surface to volume ratio is the main feature of microstructured reactors, which is in the range of 10,000–50,000 $\frac{\mathrm{m}^2}{\mathrm{m}^3}$. Usually MSR are operated under laminar flow conditions. The heat transfer coefficient values for liquids are about 10 $\frac{\mathrm{kW}}{\mathrm{m}^2\mathrm{K}}$, which is one order of magnitude higher than in the traditional heat exchangers.

The high heat transfer allows to utilize the full potential of catalysts for highly endothermic or exothermic reactions and avoid hot-spots formation. Fast heating and cooling of reaction mixtures is possible in open reactor systems (23).

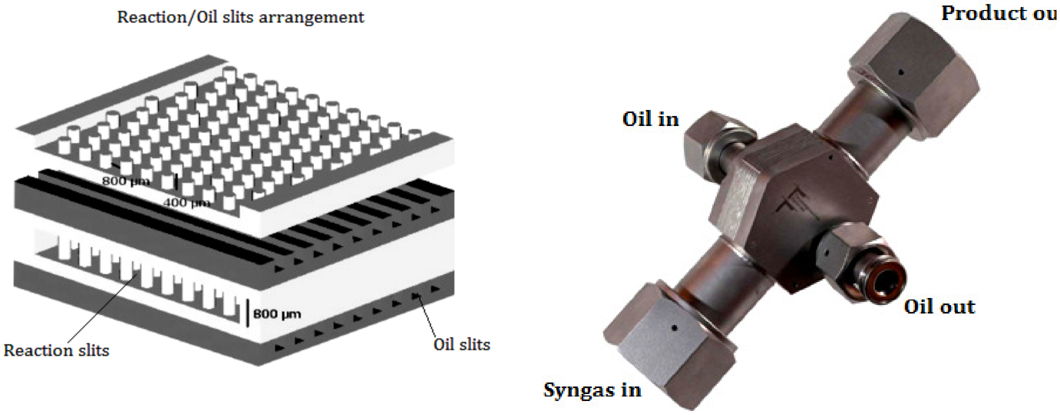

Figure 2-5: The microstructured reactor used for methanol and DME synthesis

Microstructured reactors with their small dimensions facilitate the use of distributed production units at the consumption place. This can eliminate the transport and storage of dangerous chemicals. The scale-up can be done easier when MSR units is used in parallel, without increasing the channel geometry (23).

Table 2-4: Advantages and disadvantages of microstructured reactors (22; 23; 24)

Advantages	Disadvantages
Compactness	Scale-up (economy of scale-up)
Operation at high pressure	
Good heat and mass transfer	
Inherent safety	
Thermal behavior (isothermal)	
Negligible pressure drop and diffusion limitations	
short residence times	

In summary, microstructured reactors lead to (23): process intensification, inherent reactor safety, broader reaction conditions including up-to the explosion regime, distributed production, faster process development. These make MSR suitable for fast, highly exothermic or endothermic chemical reactions.

2.2 Catalysts for DME synthesis

2.2.1 Methanol synthesis catalysts

Several catalysts were used for methanol synthesis reaction. In 1923, BASF developed the first catalyst with ability to synthesis of large amounts of methanol. The process operated at high pressure and temperatures (300 bar&300–400°C) and over a Zn/Cr_2O_3 catalyst. In 1966, Zn/Cr_2O_3 catalyst replaced by a more active catalyst: $Cu–ZnO–Al_2O_3$, developed by ICI, which made it possible to operate at much milder condition (60–80 bar and 250–280°C)(25). Industrially, Cu–ZnO-Support is the most common methanol synthesis catalyst. Al_2O_3 is the most common support and as a structural promoter. Zinc oxide has very low activity for methanol synthesis but enhances the activity of copper catalyst. Nakamura et al. suggested that Zn atoms also act as a chemical promoter (25).

The supported Pd catalyst for synthesis of methanol has been studied extensively and showed a more stable activity compare to the Cu-based catalyst. Cu-based catalyst at high temperature and in the presence of H_2O and CO_2 deactivates quickly with time on stream (26).

2.2.2 Methanol dehydration catalysts

The reaction (2-3) is catalyzed by the dehydration catalysts. The reaction is very selective and the formation of by-products is too low. The strength and type of the acid sites varies between the different suppliers or technologies. Both Brøndsted and Lewis acid sites are active. The key point for the catalyst is to have a sufficiently high acidity in order to have a high activity but without having coke formation to avoid rapid catalyst deactivation (12).

The kinetic models, mostly, are based on the Langmuir-Hinshelwood mechanism and the rate-limiting step is considered to be the reaction between the two adsorbed methanol molecules. Numerous catalysts have been suggested. The different acid function were studied such as: promoted alumina, zeolite-based materials and a silico-alumino-phosphates (SAPO). Industrially, the most important catalyst is based on aluminium oxide or aluminium silicates with or without promoters (12).

$\gamma - Al_2O_3$

$\gamma - Al_2O_3$ with good thermal and mechanical stability has a porous amorphous structure. $\gamma - Al_2O_3$ as a solid-acid catalyst that can be used for DME production, offers (25):

- Acidity
- High surface areas (50–300 $m^2\ g^{-1}$)
- Mesopores of between 5 and 15 nm
- Pore volumes of about 0.6 $cm^3\ g^{-1}$
- High thermal stability
- The ability to be shaped into mechanically stable extrudates and pellets.

Zeolites

Zeolites with their acid sites are catalytically active in the hydrocarbon reactions. The pore system affects the selectivity of reactions by excluding both the participation and formation of molecules that are too large for the pores. The zeolite contains channels and cages where cations, water and adsorbed molecules may reside and react. The specific absorption properties of zeolites such as their acidity makes them attractive catalysts (25).

“Synthetic zeolites are usually named after the industry or university where they were developed, e.g. ZSM stands for Zeolite Socony Mobil. With over 600 currently known zeolites and new ones discovered every year, it is useful to have a general classification of structures endorsed by the IUPAC. In this system, each structure has three letters, for example MFI for ZSM-5” (25).

Compensating Cations and Acidity: When Al^{3+} replaces Si^{4+} ions atoms in the tetrahedra, the units have a net charge of –1, and hence cations such as Na^+ are needed to neutralize the charge. The number of cations present within in a zeolite structure equals the number of alumina tetrahedral in the framework. Thus, for the case of ZSM-5 its sodium compensated form is indicated as Na-ZSM-5 (Na-X). If the sodium ions are replaced by protons would be as H-ZSM-5 (H-X), the zeolite becomes a gigantic polyacid.

Zeolites offer (25):

- Cristallinity
- Microporosity
- Uniform pore systems
- Pore channels or cages
- High internal surface area
- High thermal stability
- Ion exchange capabilities
- Acidity
- Nontoxic
- Environmentally safe

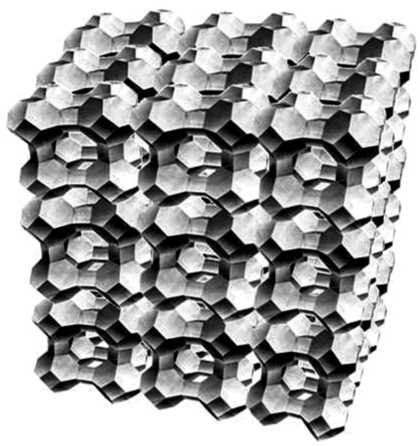

Figure 2-6: The structure of a zeolite

2.2.3 Bifunctional catalysts

In the current study, the term "*bifunctional catalyst*" is used to refer to a catalysts mixture that possesses two catalytic sites, which is capable of catalyzing methanol synthesis and methanol dehydration reactions. A good characteristic of bifunctional catalyst is to exhibit *synergistic effect* in such a way each catalyst enhances the activity of the other. The direct process for synthesis of DME requires a bifunctional catalyst based on the methanol synthesis catalyst combined with an acid function. A collection of bifunctional catalysts with different contents and additives has been studied for the direct DME synthesis. In the following several catalysts and the effect of additives is summarized.

Acid strength of solid acid catalyst

The methanol dehydration rate is dependent on the acid strength of the solid acid catalysts. J.H. Kim et al.(27) studied methanol dehydration over NaZSM-5 and HZSM-5 with the acid strength order of:

HZSM-5(30) >HZSM-5(50) >HZSM-5(100) ≈NaZSM-5(30) >NaZSM-5(50) >NaZSM-5(100)

The admixed catalysts with HZSM-5(30) show the highest activity in the direct DME synthesis and the catalysts with NaZSM-5(100) show no DME in the products.

The CO conversion for the catalysts with NaZSM-5(50) is not so much different from that for NaZSM-5(30), but the DME yield of catalysts with NaZSM-5(30) is much higher than that for NaZSM-5(50).

K.S. Yoo et al.(28) was studied the role of solid acid catalyst for methanol dehydration and direct DME production from synthesis gas. In the methanol dehydration, the strength of acid sites affected significantly catalytic performance due to the formation of solid carbon (coke) leading to the catalytic deactivation.

The superiority of ferrierite over the other zeolites

P.S. Sai Prasad et al. (29) was studied four different physical mixture of catalysts containing Cu–ZnO–Al_2O_3 (common methanol synthesis catalyst) and ferrierite, ZSM-5, NaY or HY, as the solid acid component in direct synthesis of DME.

The results show that Cu–ZnO–Al_2O_3/ferrierite gives higher CO conversion and DME selectivity because of facile reducibility of the metal component, suitable topology, proper acidic strength and resistance towards catalyst deactivation. Table 2-5 shows that dehydration activity of ZSM-5 and NaY supported catalysts, is lower than the other two catalysts. The Y supported bifunctional catalyst shows very high selectivity (57.2%) towards carbon dioxide.

Table 2-5: Conversion and products distribution on bifunctional catalysts (29).

Catalyst	CO conv. (%)	Selectivity (mol%)			
		DME	Methanol	HC	CO_2
CZA-FER	30.2	28.7	42.8	0.7	27.8
CZA-ZSM-5	13.9	14.4	64.1	0.6	20.9
CZA-NaY	14.6	12.5	71.7	0.6	15.2
CZA-Y	22.7	29.7	12.5	0.6	57.2

[a] The averaged values for CO conversion and selectivity are taken in the range of 12–15 h on stream.

Reaction conditions: $T = 250$ °C, $P = 4$ MPa, CO/CO_2/H_2 =41/21/38 (vol.%), GHSV = 5500 mL h^{-1} g_{cat}^{-1}

The effect of ZrO_2

A series of CuO/ZnO/ZrO_2/HZSM-5 with different ZrO_2 contents were evaluated by K. Sun et al. (30). The bifunctional catalysts were prepared by coprecipitation sedimentation method. The addition of ZrO_2 exhibited a strong effect on the CO conversion and DME yield. The optimum amount of 8% wt. of ZrO_2 was obtained.

The optimized catalyst (Table 2-6) showed a good catalytic activity with high DME selectivity (83.12%) and good CO conversion (72.79%).

Table 2-6: Effect of ZrO_2 contents on the catalytic performance for direct synthesis of DME (30).

Catalyst	CO conversion (%)	DME selectivity (C-mol %)	DME yield (C-mol %)
CZZ/H-0	42.81	45.70	19.56
CZZ/H-2	57.63	74.99	43.22
CZZ/H-4	67.25	79.07	53.17
CZZ/H-8	**72.79**	**83.12**	**60.50**
CZZ/H-10	71.57	82.50	59.04
CZZ/H-14	69.56	82.69	57.52

Reaction conditions: T = 250 °C, P = 3 MPa, H_2:CO:CO_2 = 67:30:3 (vol.%), GHSV = 1500 mL h^{-1} g_{cat}^{-1}

The effect of Sb_2O_3

D. Mao et al. (31) studied the effect of Sb_2O_3 on catalytic performance of bifunctional catalysts (Prepared by physical mixing). As indicated in Table 2-7, after Sb_2O_3 modification of HZSM-5, the hydrocarbon by-products and CO_2 was significantly decreased. The Sb_2O_3 contents of more than 5 wt% did not improve the performance of the catalyst remarkably. On the other hand, the modification of HZSM-5 with Sb_2O_3 did not affect the CO conversion.

Table 2-7: Effect of Sb_2O_3 content on catalytic performance of the admixed catalyst of CuO–ZnO–Al_2O_3 and antimony oxide modified HZSM-5 zeolite (31).

Sb_2O_3 (%)	CO conversion (%)	Selectivity (%)				DME yield (%)
		DME	Methanol	HC	CO_2	
-	95.2	55	3.3	9.3	32.4	52.4
5	95	67.6	3.3	1.2	27.9	64.2
10	95	68.2	3.3	0.96	27.5	64.8
20	95	69	3.2	0.58	27.2	65.6
30	95.1	68.7	3.2	0.67	27.4	65.3

Reaction conditions: T = 260 °C, P = 4 MPa, H_2:CO:CO_2:N_2 = 61.4:28.5:2.8:7.3 (vol.%), GHSV = 1500 mL h^{-1} g_{cat}^{-1}.

2.2.4 Preparation methods of bifunctional catalysts

Q. Ge et al. (32) investigated the effects of preparation methods on catalytic performance and the structures of bifunctional catalysts.[1] The bifunctional catalysts is containing CuO/ZnO/A1$_2$O$_3$ and $\gamma-Al_2O_3$ catalysts that prepared by seven different methods.

I. Coprecipitation method: "A solution of $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ and a solution of Na_2CO_3 were coprecipitated when added to H_2O simultaneously and dropwise over a period of 30 min at 70°C, pH=7 under continuous stirring. The precipitates formed were further aged for an hour under stirring at the same temperature. The precipitates were then filtered out, washed and dried at 120°C for 4 h, then calcined in N_2 at 350°C for 6 h ".

II. Slurry mixing method: "A solution of $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$ and a solution of $Al(NO_3)_3.9H_2O$ were coprecipitated separately with a solution of Na_2CO_3 when added to H_2O simultaneously and dropwise over a period of 30 min at 70°C under continuous stirring. Both the precipitates formed were aged for an additional hour under stirring at the same temperature. Then both precipitates were filtered, washed and mixed with each other when added to H_2O. Mixed precipitates were continuously stirred for 30 rains and then filtered, dried and calcined" .

IlL Impregnation method: "The CuO/ZnO/Al_2O_3 catalysts were prepared by impregnation of $\gamma-Al_2O_3$ with a comparable volume of copper and zinc nitrate solution. The soaked paste was dried at 12°C, ground and fired in N_2 at 350°C for 6 h".

IV. Coprecipitating impregnation method: "Copper, zinc and aluminium nitrate solution and sodium carbonate solution were coprecipitated when added $\gamma-Al_2O_3$ and H_2O suspended liquid simultaneously and dropwise ".

V. Coprecipitating sedimentation method: "Copper, zinc and aluminium nitrate solution and sodium carbonate solution were coprecipitated when added to H_2O simultaneously and dropwise over a period of 30 rain at 70°C, pH=7 under continuous stirring. The precipitates which formed were aged for an additional hour under stirring

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[1] A fixed-bed microreactor is used to evaluate catalytic synthesis of DME from synthesis gas at a pressure of 4.0 MPa and a GHSV of 1500 h^{-1}.

at the same temperature. The precipitates were then filtered, washed and added to the suspended liquid including dehydration component and water. The mixtures were stirred, filtered, dried, and calcined “.

VI. Wet mixing method: “Dried coprecipitates and $\gamma - Al_2O_3$ were mixed in water, stirred, filtered, dried, calcined”.

VII. Dry mixing method: “Calcined coprecipitates and $\gamma - Al_2O_3$ were mixed and ground “[28].

The contact separation of the two kinds of active sites in bifunctional catalysts becomes shorter step by step from methods VII to I. According to their result *coprecipitate sedimentation method* is better preparation method among the other methods for direct conversion of synthesis gas to DME.

Table 2-8: Effect of preparation methods on traditional methanol synthesis catalyst (32).

Preparation method	CO conv. (%)	Selectivity (mol%)				DME/organic products(mol%)
		DME	MeOH	HC	CO_2	
I	3.1	39.1	26.4	23.5	16.1	46.6
II	3.1	26.8	44.6	9.2	19.3	33.2
III	15.9	67.1	15.9	2	15	78.9
IV	58.6	77.8	8.2	1.8	12.2	90.7
V	**82.2**	**85**	**0.7**	**1.3**	**13**	**96.4**
VI	70.3	84.1	2.5	.8	12.7	96.3
VII	63.1	81.4	5.1	0.5	13.1	93.6

Reaction conditions: T = 290 °C, P = 4 MPa, H_2:CO=2 and 5% CO_2 , GHSV = 1500 mL h^{-1} g_{cat}^{-1}.

To prepare catalysts with good catalytic activities, Q. Ge et al. recommended the following suggestion: 1) The two kinds of active centres, should have a close contact and exhibit 'synergistic effect'. 2) One kind of active centres should not cover another active centre. 3) In order to avoid the formation of new inactive chemical species, each component should not react with any other components.

2.3 Catalyst deactivation

Under normal operating conditions, and using traditional methanol catalyst as a methanol synthesis function, the catalyst has a relatively long lifetime of a few years. However, the catalyst is very sensitive to sulfur poisoning and the ZnO component in the catalyst is reacting with it to form Zn sulfide and sulfate, thus desulfurization for the feeds with significant sulfur content is necessary (33).

Sintering of the catalyst at high temperatures is another deactivation mechanism, especially at above 300°C because of the growth of the Cu crystallites and the resulting loss of catalytically active area (33).

K.S. Yoo et al.(28) reported that in the methanol dehydration, the strength of acid sites affected catalytic performance by coke formation leading to the catalytic deactivation. The mild acid sites are responsible mainly for simple dehydration process and do not allow the formation of solid carbon. Moreover, the pore structure of the catalyst is an important factor to maintain the catalytic stability. For example, SAPO-34 and -18, with unfavorable pore structure and acidity, were deactivated by accumulating carbonaceous material inside their supercages. But SAPO-11 and -5 due to the lack of pore expansions prevented to some extent the formation of large carbonaceous materials.

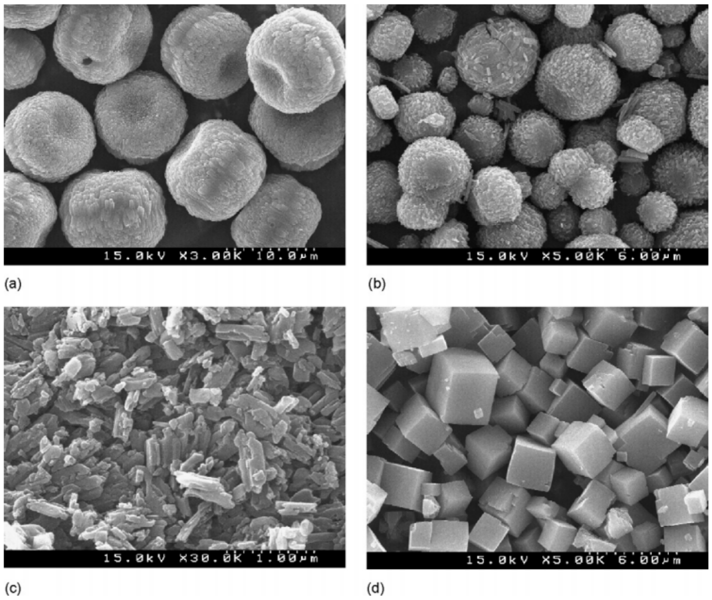

Figure 2-7: SEM image of various SAPO catalysts: (a) SAPO-5; (b) SAPO-11; (c) SAPO-18; (d) SAPO-34 (28)**.**

D. Wang et al. (17) was studied the effect of H_2O on bifunctional catalyst in direct slurry phase DME synthesis. A commercial methanol synthesis catalyst and a γ-Al_2O_3 under reaction conditions of 260 °C and 5.0 Mpa were tested. It was found that the Cu-based catalyst was less stable compare to under methanol synthesis conditions. The results indicated that H_2O, which is formed in DME synthesis, caused high deactivation rate of the Cu-based catalyst. Crystallite size growth of Cu, metal loss of Zn and Al, formation of $Cu_2(OH)_2CO_3$ and $Zn_5(OH)_6(CO_3)_2$ and carbon deposition were the possible reasons for the high deactivation rate of the Cu-based catalyst.

2.4 Catalyst characterization

The different analytical activities are used to find a detailed chemical and structural picture of the catalysts. The information obtained can be used to develop a better understanding of the function of a catalyst, which it seems to be necessary for the improvement of existing catalysts and the formulation of new ones (34).

2.4.1 Nitrogen physisorption

Physisorption, also called physical adsorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption. Measurements of gas adsorption isotherms are widely used for determining the surface area and pore size distribution of catalysts. Non-specific Brunauer-Emmett-Teller (BET) method is a standard procedure to measure surface areas. The use of nitrogen as the adsorptive gas is recommended if the surface areas are higher than 5 m^2/g (35). Nitrogen adsorption at 77 K is widely used for the determination of the surface area and pore size distribution of various porous materials. The Brunauer, Emmett and Teller (BET) adsorption isotherm equation(36):

$$\frac{1}{\left[V_a\left(\frac{P_0}{P}-1\right)\right]}=\frac{C-1}{V_mC}\times\frac{P}{P_0}+\frac{1}{V_mC} \tag{2-5}$$

Where:

P: is partial vapour pressure of adsorbate gas in equilibrium with the surface, $[Pa]$

P_0: is saturated pressure of adsorbate gas, $[Pa]$

V_a: is volume of gas adsorbed at standard temperature and pressure (STP) , $[mL]$

V_m: is volume of gas adsorbed at STP to produce an apparent monolayer on the surface, $[mL]$

C: is dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas

Then the BET value ($\frac{1}{\left[Va\left(\frac{P_0}{P}-1\right)\right]}$) is plotted against $\frac{P}{P_0}$. This plot should yield a straight line usually in the approximate relative pressure range 0.05 to 0.3. From the resulting linear plot, the slope, which is equal to $\frac{C-1}{V_m C}$, and the intercept, which is equal to $\frac{1}{V_m C}$ are evaluated by linear regression analysis. From these values, $V_m$can be calculated easily. Following equation gives the specific surface area(36):

$$S_B = \frac{V_m . N . a}{m \times 22400} \tag{2-6}$$

If the adsorbate is nitrogen : $S_B = 4.35\ V_m$ (2-7)

Where:

S_B: is specific surface area, $[\frac{m^2}{g}]$

m: is the mass of test powder, $[m]$

a: is effective cross-sectional area of one adsorbate molecule, $[nm]$

N: is Avogadro constant ($6.022 \times 10^{23}\ mol^{-1}$)

In addition, Pore size distribution of catalysts can be calculated according to the Barrett-Joyner-Halenda (BJH) method.

2.4.2 X-ray diffraction (XRD)

X-ray dif-fraction (XRD) is one of the oldest and most frequently applied techniques in catalyst characterization. X-rays have wavelengths in the Angstrom range, and they have sufficient energy to penetrate solids and to probe their internal structure. Each crystallographic phase has a unique diffracted pattern. In catalyst characterization, diffraction patterns are used to identify the crystallographic phases that are present in the catalyst and to obtain an indication of particle size. A conventional X-ray source consists of a target that is bombarded with high-energy electrons. The emitted X-rays arise from two processes. Electrons slowed down by the target emit a continuous background spectrum of Bremsstrahlung(37).

X-ray diffraction is the elastic scattering of X-ray photons by atoms in a periodic lattice. Fig.2-8 illustrates how diffraction of X-rays by crystal planes allows one to derive lattice spacings by using the Bragg relationship(37):

$$n\lambda = 2d.\sin\theta; \quad n = 1, 2, 3, \ldots \tag{2-8}$$

Where:

λ is the wavelength of the X-rays;
n is the integer called the order of the reflection.
d is the distance between two lattice planes;
θ is the angle between the incoming X-rays and the normal to the reflecting lattice plane;

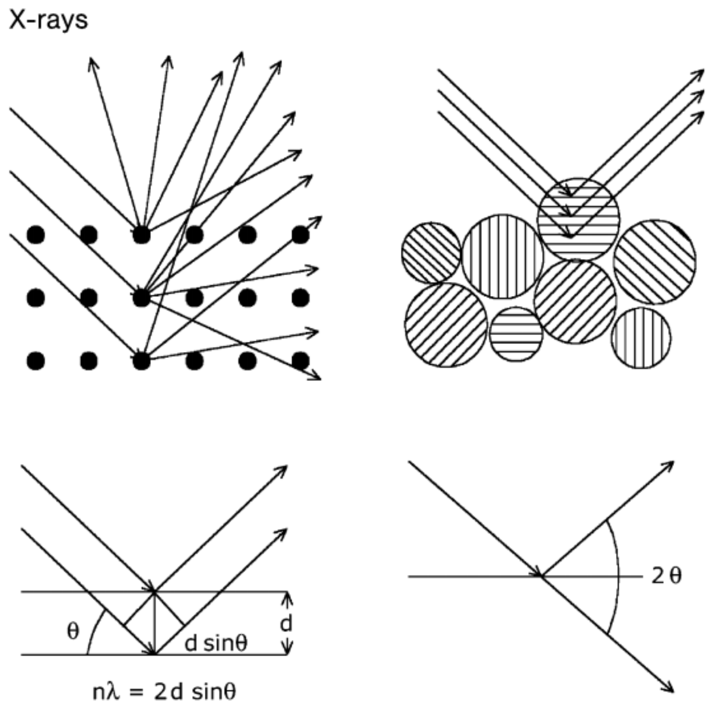

Figure 2-8: X-rays scattered by atoms in an ordered lattice interfere constructively in directions given by Bragg's law. (37)

A stationary X-ray source (usually Cu Kα) with a movable detector, which scans the intensity of the diffracted radiation as a function of the angle 2θ between the incoming and the diffracted beams, can measure the XRD pattern of a powdered sample. Rotating powders during measurement enhances the fraction of particles that contributes to the diffraction pattern.

XRD can also determine the crystallite size. Scherrer equation can give the mean size of the ordered (crystallite) domain:

$$< L > = \frac{K\lambda}{\beta.\cos\theta} \tag{2-9}$$

Where:

$< L >$	is a measure for the dimension of the particle in the direction perpendicular to the reflecting plane;
λ	is the wavelength of the X-rays;
K	Is a constant (Often taken as 1).
β	is the peak width;
θ	is the angle between the incoming X-rays and the normal to the reflecting lattice plane;

3 EXPERIMENTAL

3.1 Catalyst preparation

CuO–ZnO–Al_2O_3 was prepared (38) by co-precipitation of the metal nitrates with sodium carbonate at pH=7.

3.1.1 Materials

The chemicals used for synthesis of methanol catalyst were cupric nitrate pentahydrate[1] [$Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$], zinc nitrate hexahydrate[1] [$Zn(NO_3)_2 \cdot 6H_2O$], and aluminium nitrate nonahydrate[1] [$Al(NO_3)_3 \cdot 9H_2O$], sodium carbonate[1] [Na_2CO_3] and sodium acetate[1] [CH_3COONa].

3.1.2 Procedure

The catalyst was prepared according to the following scheme (38):

- Three solutions were prepared:
  - Metal solution: 15.95g $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$ + 29.62g $Zn(NO_3)_2 \cdot 6H_2O$ + 21.43g $Al(NO_3)_3 \cdot 9H_2O$ dissolved in 100 mL deionized water.
  - Sodium carbonate solution: 27.03g Na_2CO_3 dissolved in 200 mL deionized water.
  - Sodium acetate solution: 4.1g CH_3COONa dissolved in 50 mL deionized water.

➢ The sodium acetate solution was heated using overhead stirrer in large bucket to 50°C. Metals and sodium carbonate solution were added dropped wise and simultaneously, using two peristaltic pumps, to the sodium acetate solution with continous stirring and keeping the temperature at 50 °C and pH=7.0 over about 2 hours. After completing the addition, stirring was continued for 1 hour.

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[1] provided from Sigma-Aldrich Fluka

- Stirring was stopped and precipitate allowed to settle. The precipitate was separated by filtration using a medium Buchner funnel with vacuum.The precipitate is washed with numerous portions of deionized water at room temperature to remove sodium.

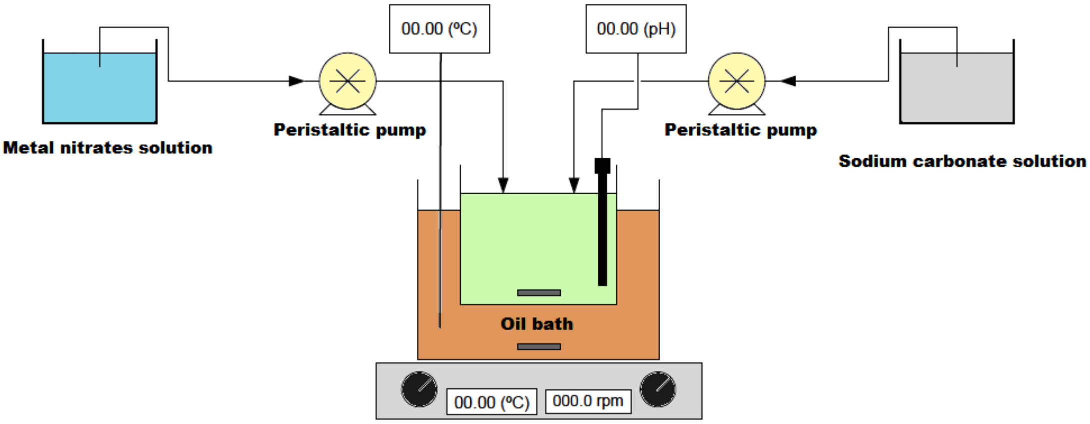

Figure 3-1: Schematic of catalyst coprecipitation process.

- The precipitate was placed on a ceramic tray and dried in a forced air oven at 110ºC for 16 hours. A portion of the dried sample was calcined in a glassy calcination reactor under flowing of certain flow rate of air, which was calculated based on catalyst weight. Table 3-1 shows the applied temperature program.

Table 3-1: The temperature program for calcination

1.	25 ° C to 400 ° C over 2 hours
2.	Hold at 400 ° C for 2 hours
3.	Cool to 25 ° C over about 2 hours

$HZSM-5$ was used as methanol dehydration catalyst. The catalysts were sieved to 50–80 µm size fractions and then mixed with different mass ratios, which are shown in Table 3-2.

Table 3-2: The catalysts composition

	Methanol synthesis catalyst (gr)		Methanol dehydration catalyst (gr)		Total weight (gr)
	$CuO/ZnO/Al_2O_3$				
	Commercial	Homemade	$\gamma-Al_2O_3$	$HZSM-5$	
Ratio=1	-	0.5	-	0.5	1
Ratio=2	-	0.666	-	0.334	1
Ratio=4	-	0.8	-	0.2	1
Ratio=6	-	0.857	-	0.143	1
Ratio=8	-	0.889	-	0.111	1

3.2 Catalyst characterization

In the current study, Nitrogen physisorption and X-ray diffraction were used for catalyst characterization.

3.2.1 N_2 physisorption

The pore size distribution based on BJH (Barrett-Joyner-Halenda) calculations, the micropore fraction (t-plot analysis) and the BET (Brunauer-Emmett-Teller) surface area of the catalysts were measured by physisorption measurements of nitrogen at -196 ºC using a Micrometrics Tristar 3000 instrument. Prior to BET analysis the samples were placed into the sample tubes and outgassed at 200ºC for 8 hours.

3.2.2 X-ray diffraction

D8 Focus apparatus from Bruker AXS with CuKα radiation was used. The D8 Focus was equipped with a theta/theta Goniometer and a LynxEye detector. The powder samples were scanned in the 2θ-range from 20º to 70º with a step size of 0.02º and a step time of 1s.

3.3 DME synthesis set-up

3.3.1 Set-up Description

The catalytic reactions were performed in the DME synthesis set-up. This setup is designed for conversion of synthesis gas into liquids (DME). All equipments are designed for pressures up to 100 bars and temperatures up to $350^{\circ}\,C$. The test unit is equipped with three common gas feeding lines and two reactor lines: Microstructured reactor and Fixed-bed reactor. The microstructured reactor manufactured by the Institute for Micro Process Engineering (IMVT) at Karlsruhe Institute of Technology in Germany. The microstructured reactor is heated with heat transfer oil (temperatures up to $350^{\circ}\,C$), passing through the heat exchanger channels in the microchanneled reactor unit. For higher temperatures the microchanneled reactor is heated by electrical heating bands. The reactor and oil tubing were insulated to reduce any heat loss to the external sections. The temperature gradient between inlet and outlet of reactor is less than 1 K. The fixed-bed reactor is clamped inside an aluminum block and heated by a Kanthal oven. The product leaving the reactor is condensed in either a hot or a cold pot below the reactors. Several *Bronkhorst* mass flow controllers were controlled the mass flow rates and a *Bronkhorst* backpressure controller was regulated the pressure. A side stream is provided for online gas chromatography analysis of the dry product gas. After depressurizing the gases are vented.

Figure 3-2: The DME synthesis set-up.

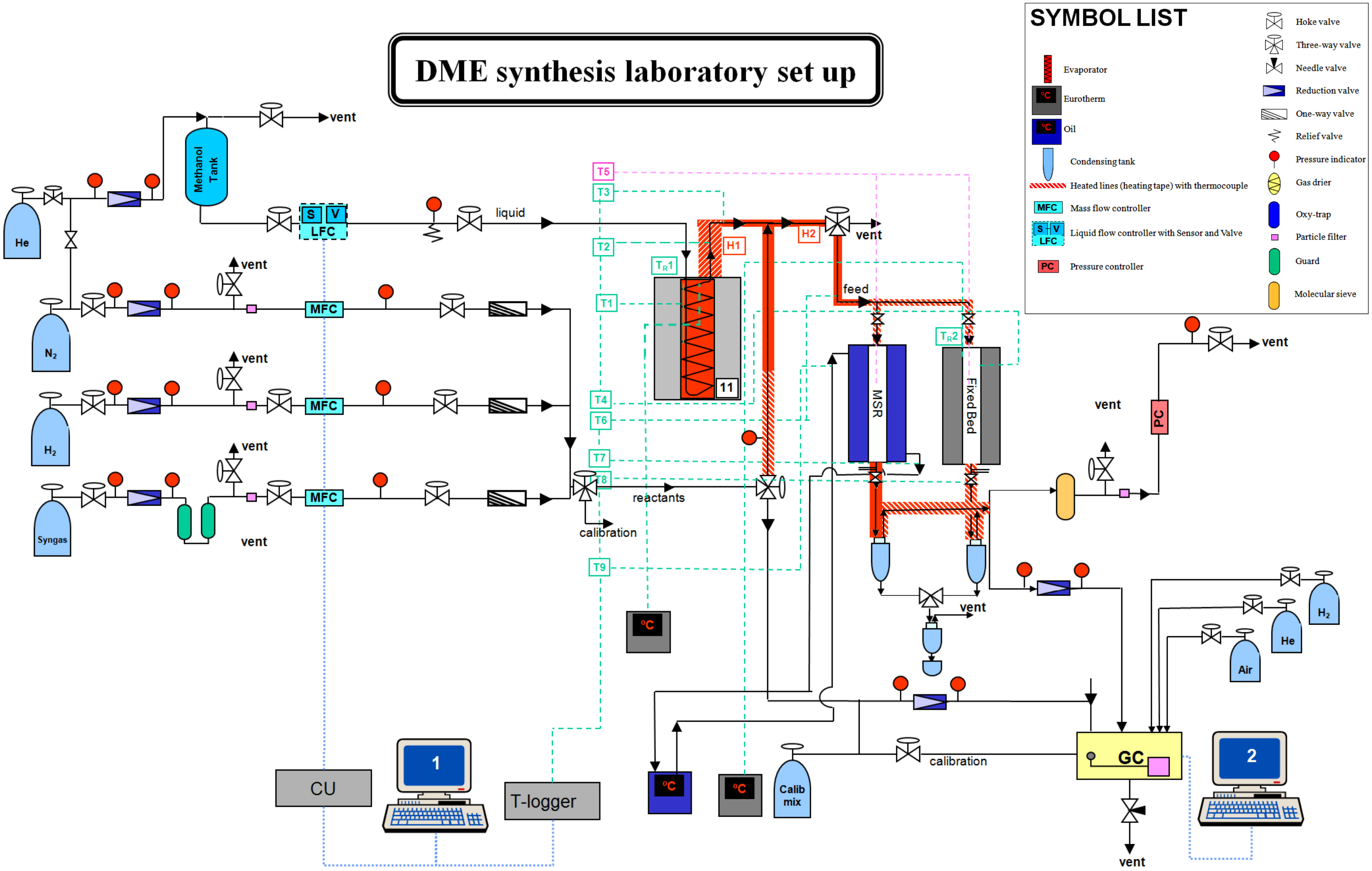

Figure 3-3: Flow diagram of DME synthesis laboratory set-up

3.3.2 Gas Chromatograph

The rig is equipped with a GC[1] for online analysis of product gas and offline analysis of liquid products. The GC is an Agilent 7890A. To avoid any condensation of products, the outlet gas lines were heated (180 °C) until entering the GC. Liquefaction of DME, methanol and water occurs at minimum partial pressure 129, 30 and 10 bars respectively at 180 °C. All products are thus present in the gas phase under the operating condition applied, and liquids were also not observed (13).

The GC equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). It was adopted to analyze the feed and product gases. The TCD was applied to analyze H_2, CO, CO_2, N_2 and CH_4. On the other hand, FID was used to analyze hydrocarbons, alcohols and oxygenates C1-C6.

The GC was calibrated for the all main components present in the feed and products. N_2 for TCD and CH_4 for FID were used as internal standards for the analysis. CO and CO_2 conversions, DME and methanol yields are based on a total carbon balance and the equations for calculations as follow:

$$X_{CO} = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} \times 100 \qquad (3\text{-}1)$$

$$X_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100 \qquad (3\text{-}2)$$

$$Y_{DME} = \frac{2F_{DME}}{\left(F_{CO,in} + F_{CO_2,in}\right)} \times 100 \qquad (3\text{-}3)$$

$$Y_{MeOH} = \frac{F_{MeOH}}{\left(F_{CO,in} + F_{CO_2,in}\right)} \times 100 \qquad (3\text{-}4)$$

Where:

X_{CO}, X_{CO_2} : CO and CO_2 conversion

Y_{DME}, Y_{MeOH} : DME and methanol yields

$F_{CO,in}$, $F_{CO_2,in}$: The molar flow rate of CO and CO_2 in the feed gas, $\frac{mol}{s}$

$F_{CO,out}$: The molar flow rate of CO in the product gas, $\frac{mol}{s}$

F_{DME} , F_{MeOH} : The molar flow rate of DME and Methanol in the product gas, $\frac{mol}{s}$

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[1] Gas Chromatograph

The peak areas from GC analysis could be converted into flow rates by starting the calculation from standard analysis gases. Since N_2 as an inert gas is not converted, thus:

$$F_{tot,in}.A_{N_2,in}.k_{N_2,TCD} = F_{tot,out}.A_{N_2,out}.k_{N_2,TCD} \tag{3-5}$$

$$F_{tot,out} = F_{tot,in}.\frac{A_{N_2,in}}{A_{N_2,out}} \tag{3-6}$$

$$F_{CO,out} = F_{tot,out}.(A_{CO,out}.k_{CO,TCD}) \tag{3-7}$$

$$F_{CO_2,out} = F_{tot,out}.(A_{CO_2,out}.k_{CO_2,TCD}) \tag{3-8}$$

$$F_{CH_4,out} = F_{tot,out}.(A_{CH_4,out}.k_{CH_4,TCD}) \tag{3-9}$$

Where:

$k_{CO,TCD}$, $k_{CO_2,TCD}$, $k_{CH_4,TCD}$: The response factor for CO, CO_2 and CH_4

$A_{CO,out}$, $A_{CO_2,out}$, $A_{CH_4,out}$: The peak area for CO, CO_2 and CH_4 in the product gas analysis.

Methane is a common component in both TCD and FID detectors, and could connect the calculation in TCD to FID.

$$(F_{tot,out}.A_{CH_4,out}.k_{CH_4})^{TCD} = (F_{tot,out}.A_{CH_4,out}.k'_{CH_4})^{FID} \tag{3-10}$$

$$(F_{tot,out})^{FID} = (F_{tot,in}.\frac{A_{N_2,in}}{A_{N_2,out}}.A_{CH_4,out}.k_{CH_4})^{TCD} \tag{3-11}$$

$$F_{DME,out} = (F_{tot,out})^{FID}(A_{DME,out}.k_{DME})^{FID} \tag{3-12}$$

$$F_{MeOH,out} = (F_{tot,out})^{FID}(A_{MeOH,out}.k_{MeOH})^{FID} \tag{3-13}$$

The procedure for the operation of the GC is explained in appendix B.

3.3.3 Gas feed system

The gas feed system has three high-pressure gas lines for syngas (H_2, CO, CO_2, N_2), inert gas (He or N_2) and H_2. Other gases, i.e. CO or CO_2 are also possible for adjusting Syngas composition. The gas feed lines are equipped with manometers, reduction valves, traps, filters, manual open/close valves and valves to ventilation.

The gas flows to the reactor and controlled by *Bronkhorst* digital mass flow controllers (DMFC) specified and calibrated for the given gases, pressures and gas flow ranges. Gas flow is adjusted by either PC or power supply/readout unit for the controllers.(The flow controller software is explained in appendix C).

3.3.4 Catalytic reaction

The experimental set-up of the high-pressure fixed-bed reactor (Fig.3-4) system used for the synthesis of DME from three different feed gases. Table 3-3 shows the composition of feed gases. A fixed amount of the catalyst was loaded in the stainless steel tube reactor.

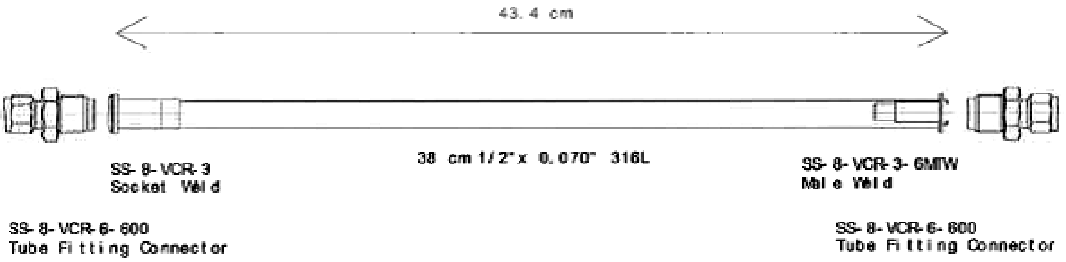

Figure 3-4: Shematic of the fixed-bed reactor used for the DME synthesis

Table 3-3: The Syngas composition

		Mol (%)				
FEED	H_2:CO	H_2	N_2	CO	CH_4	CO_2
1	1	42	5	42	6	5
2	2	56	5	28	6	5
3	4	67.2	5	16.8	6	5

3.3.4.1 Leak test

It is very important be ensured that there is no leak at any point of the lines. Not only for safety reasons, it is also very important receive representative data of the system to get coherent conclusions of the process. Leak test procedure could be as following steps:

- Load the catalyst into the reactor.
- Fix the reactor in setup
- Close the valve to the GC.
- Increase the pressure up to 10 bars (Channel nr. 4: setpoint=10%) by introducing nitrogen (Channel nr. 1: setpoint=100 %).
- As pressure controller shows steady amount of 10 bars, stop the nitrogen flow (Channel nr. 1: setpoint=0 %).
- Check the pressure drop. If pressure drop is significant (for example after 5 minutes $P \leq 9.90$ bars), introduce hydrogen (Channel nr. 3: setpoint=100%).
- Check the connections and find the leak(s) by using hydrogen detector. Tighten the related connections more, but carefully, to remove the leak(s).
- Increase the pressure up to 25 bars (Channel nr. 4: setpoint=25%) by introducing nitrogen (Channel nr. 1: setpoint=100 %).
- As pressure controller shows steady amount of 25 bars, stop the nitrogen flow (Channel nr. 1: setpoint=0 %).
- Check the pressure drop. If pressure drop is significant (for example after 5 minutes $P \leq 24.90$ bars), introduce hydrogen (Channel nr. 3: setpoint=100%).
- Check the connections and find the leak(s) by using hydrogen detector. Tighten the related connections more, but carefully, to remove the leak(s).
- Increase the pressure up to 40 bars (Channel nr. 4: setpoint=40%) by introducing nitrogen (Channel nr. 1: setpoint=100 %) and hydrogen (Channel nr. 3: setpoint=10%).
- As pressure controller shows steady amount of 40 bars, stop the nitrogen and hydrogen flows.
- Check the pressure drop and check the connections by using hydrogen detector. If there is any leak(s), tighten the connections more, but carefully, to remove the leak(s).

- Increase the pressure to 50 bars (Channel nr. 4: setpoint=50%) by introducing nitrogen (Channel nr. 1: setpoint=100 %) and hydrogen (Channel nr. 3: setpoint=10%).
- As pressure measure shows steady amount of 50 bars, stop the nitrogen and hydrogen flows.
- Check the pressure drop and check the connections by using hydrogen detector. If there is any leak(s), tighten the connections more, but carefully, to remove the leak(s).
- Decrease the pressure to atmospheric pressure and prepare the system for the reduction.

Note

This procedure is based on following assumptions:

- Channel nr. 1 is connected to the Nitrogen bottle.
- Channel nr. 2 is connected to the Syngas bottle.
- Channel nr. 3 is connected to the Hydrogen bottle.
- Channel nr. 4 is connected to the pressure controller.

3.3.4.2 Reduction of the catalyst

Prior to the reaction, the bifunctional catalyst has to be reduced in the reactor; with flow of 5% hydrogen diluted with nitrogen and with temperature programmed heating (Fig.3-5).

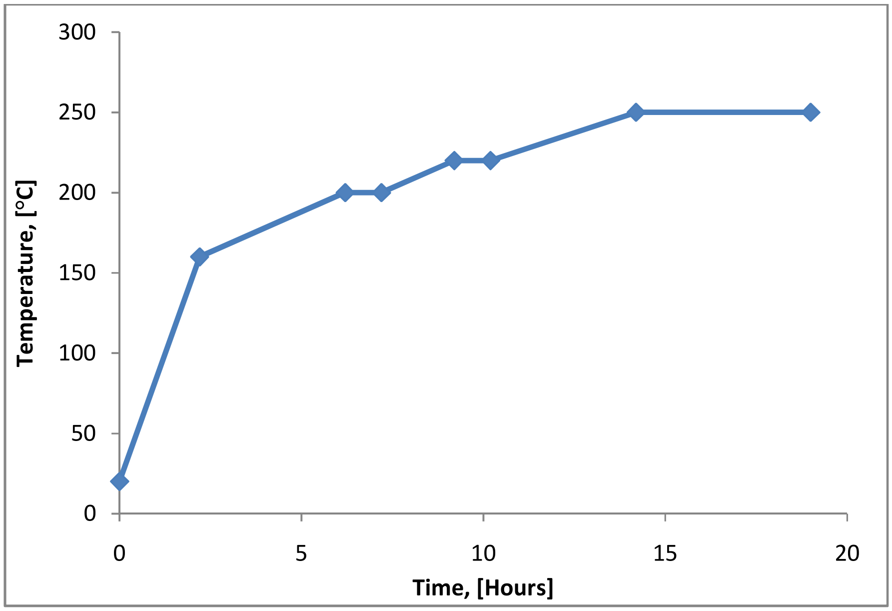

Figure 3-5: Temperature program for the reduction

The reduction can be done according the following steps:

STEP 1

Calculate total volumetric flow rate:

$$Q_{tot} = 350 \times W_{cat} \times \alpha$$

Q_{tot}: Total volumetric flow, $\frac{\text{nml}}{\text{min}}$

W_{cat}: Weight of the catalyst, gr

α: Fraction of Cu – based catalyst in the catalyst mixture

Example: $\begin{cases} \text{CuO/ZnO/Al}_2\text{O}_3 \\ \gamma - \text{Al}_2\text{O}_3 \end{cases}$ Ratio: $2:1 \rightarrow \alpha = \frac{2}{3}$ Ratio: $1:1 \rightarrow \alpha = \frac{1}{2}$

STEP 2

Calculate nitrogen and hydrogen volumetric flow rates:

$$Q_{N_2} = 0.95 \times Q_{tot}$$

$$Q_{H_2} = 0.05 \times Q_{tot}$$

Q_{N_2}: Nitrogen volumetric flow, $\frac{\text{nml}}{\text{min}}$

Q_{H_2}: Hydrogen volumetric flow, $\frac{\text{nml}}{\text{min}}$

STEP 3

Calculate nitrogen and hydrogen setpoints for Flow Controller from the calibration curves:

$$Q_{N_2} \rightarrow P_{N_2}$$

$$Q_{H_2} \rightarrow P_{H_2}$$

STEP 4

Introduce nitrogen and hydrogen according to the set points.

STEP 5

In case of fixed-bed reactor as for my experiments

Use Eurotherm to apply the temperature program (See appendix D).

With 7 steps:

- Increase to 160°C in 2.2 hours.
- Increase to 200°C in 4 hours.
- Keep at 200°C for 1 hour.
- Increase to 220°C in 2 hours.
- Keep at 220°C for 1 hour.
- Increase to 250°C in 4 hours.
- Keep at 250°C for long time (for example 99 hours).

In case of microstructured reactor

Use High temperature circulator to apply the temperature program (See appendix E).

3.3.4.3 Start the experiment

- Open the valve to the GC
- Connect all electric bans
- Start introducing Syngas (Increase the pressure up to the experiment pressure, for example 50 bars, gradually)
- Calculate feed (syngas) volumetric flow rate.
- Calculate feed setpoint for Flow Controller from the calibration curves.
- Set the temperature
    - If Microstructured reactor is used: according to the procedure for using High temperature circulator.
    - If Fixed-bed reactor is used: according to the Eurotherm's manual.
- Run GC according to the Procedure for using GC

3.4 HES

As indicated in the NTNU goals of Health, Environment and Safety, the work and learning environment must support and promote its users' capacity to work and learn, safeguard their health and well-being, and protect them against work-related illnesses and accidents. HES-related problems should be solved consecutively at the lowest possible level, in order to prevent employees or students from developing work-related illnesses or suffering work-related accidents, and to prevent the activities from having a negative impact on the environment.

Risk assessment is an important tool for a chemical process operation which is the determination of quantitative or qualitative value of risk related to a concrete situation and a recognized hazard. A risk assessment must be carried out prior to the commencement of a specified chemical process and again when the process is modified. This risk assessment is done to remove or control the risk factors during the operational period of the chemical process.

The activities associated with several HES issues on the DME synthesis set-up are:

• Transport and mounting of the gas bottle

- Modification and maintained of experimental set-up
- Leak testing and reactor installing
- Reaction experiment
- Experiment shutdown and uninstalling of reactor
- Cleaning the reactor
- Catalyst synthesis
- Handling of the catalyst

For existing risk assessments, safety measures, rules and procedures are as follows:

- In the DME synthesis set-up, a well established toxic and flammable gas alarm system is exist. So in the case of leak, the gas alarm system will able to inform and necessary action concerning the HES can be taken according to rules and procedure.
- For personal protection, safety goggle is very important in the VTL lab and it is mandatory for everyone who is working inside the lab.
- Leak test is an important procedure for decreasing the risks related to the toxic and combustible gases.

The HES assessment identification process, risk assessment and HES action plane for DME synthesis set-up are shown in appendices H and I.

The main risk concerning with toxic and combustible gases

Risk concerning with carbon monoxide (See appendix J): Carbon monoxide is a colorless and odorless gas, it comes as synthesis gas component for DME synthesis. The chemical company YARA PRAXAIR is supplier of synthesis gas in our lab. Carbon monoxide is extremely flammable and toxic. It may cause harm to the unborn child and danger of serious damage to health by prolonged exposure through inhalation. This gas should be keeping away from the source of ignition and should be store in safe area as the condition of flammable gas storage. It needs to use in well ventilated area and in case of fire, this gas should be allowed to burn if flow cannot be shut off immediately and need to immediate contact responsible person. It has not any significant effect or critical hazards environmentally. This gas should be disposed as hazardous waste.

Risk concerning with Hydrogen (See appendix J): Hydrogen is a colorless and odorless gas and extremely flammable gas, stable under recommended storage and condition. Inhalation of vapor may cause dizziness, an irregular heartbeat, narcosis, nausea or asphyxiation. If anyone inhaled, remove to fresh air. This substance classified with a health or environmental hazard. This gas should be disposed as hazardous waste. This gas should be keeping away from the source of ignition. Personal protection is necessary like goggles, apron, vent hood and protective gloves in used area and it needs to use in well ventilated area.

Risk concerning with Methanol (See appendix J): Methanol is very dangerous poison and its vapor also harmful to human. it may causes blindness if swallowed and harmful if inhaled or absorbed through skin. It may causes irritation to skin, Eyes and respiratory tract. It also affects central nervous system and liver. The liquid and vapor of methanol is flammable. Personal protection is necessary like goggles, apron, vent hood and protective gloves in used area. This liquid is slightly toxic for aquatic life and it causes degradation in soil and air. This gas should be disposed as hazardous waste. This gas/liquid should be keeping away from the source of ignition and should be store in safe area as the condition of flammable gas/liquid storage. It needs to use in well ventilated area. More information about detailed material safety data sheets are shown in appendix K.

3.4.1 Gas Warning System

Gas warning system protects lives and health by monitoring the atmosphere inside the rig and triggering an optical and acoustic alarm, as soon as the concentration of the gas (**Hydrogen** and **Carbon monoxide**) that is being monitored exceeds the preset threshold level.

Figure 3-6: Overview of the Gas warning system (External and Internal views)

When alarm starts, first of all we have to turn off the alarm. Secondly, solve the problem (Sometimes experiment has to be stopped).

Procedure for stopping the Gas warning system:

STEP 1

Shift the button to the right (As shown in Fig 3-22) and wait for the **point** (for example **point 2-** Fig 3-23**).**

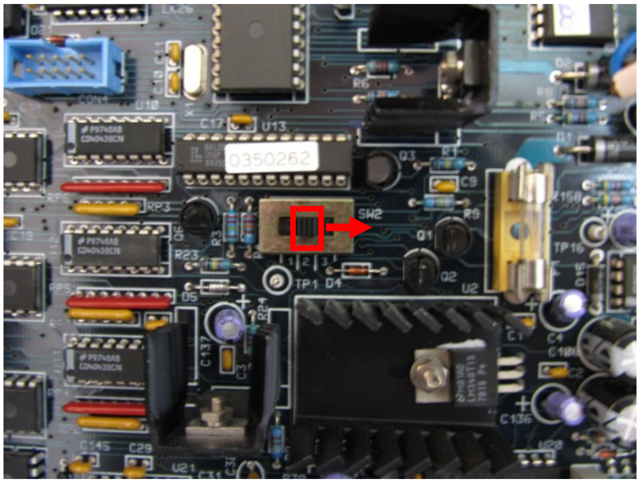

Figure 3-8: Shift the button to the right

Figure 3-7: Gas alarm system monitor

STEP 2

Press **[SEL]** and then press **[INH]**.

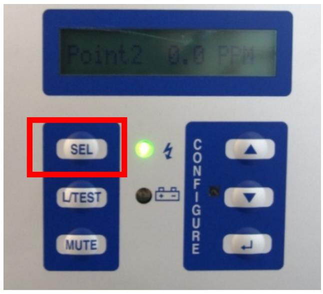

Figure 3-9: Press SEL

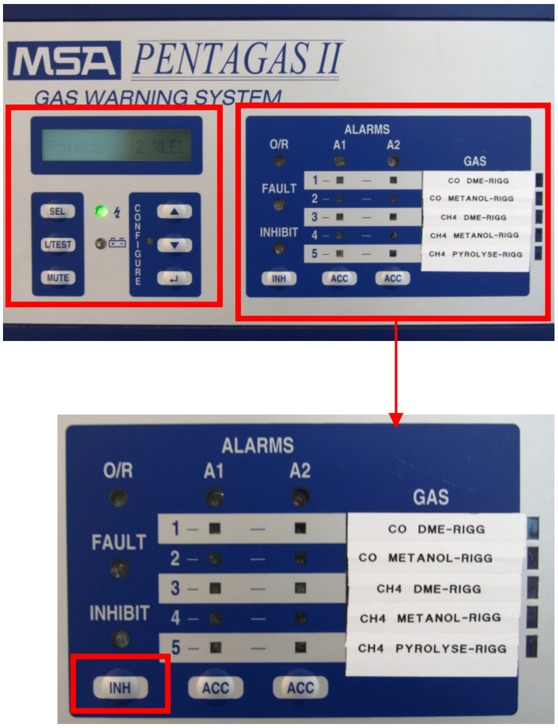

Figure 3-10: Press INH

4 RESULTS AND DISCUSSION

4.1 Catalyst characterization

4.1.1 N_2 physisorption

Table 4-1 shows the BET surface area of some of the catalysts. The result shows high surface area for HZSM-5. According to this fact, it will be possible to have a good catalyst mixture with high ratio of CuO-ZnO-Al_2O_3:HZSM-5. More result of the N_2 physisorption can be found in the appendix F.

Table 4-1: BET surface area of the catalysts

Catalyst	BET surface area (m^2/g)
CuO-ZnO-Al_2O_3(Homemade)	56
HZSM-5	344
CuO-ZnO-Al_2O_3: HZSM-5=1	192
CuO-ZnO-Al_2O_3: HZSM-5=2	149
CuO-ZnO-Al_2O_3: HZSM-5=4	109

4.1.2 X-ray diffraction

Fig.4-1 shows the XRD pattern of CuO-ZnO-Al_2O_3:HZSM-5=2 catalyst. It can be concluded that ZnO is the major component in crystal form. CuO and Cu are the other components. The diffraction patterns confirm that during reduction and reaction the most of CuO disappeared and probably reduced to form Cu.

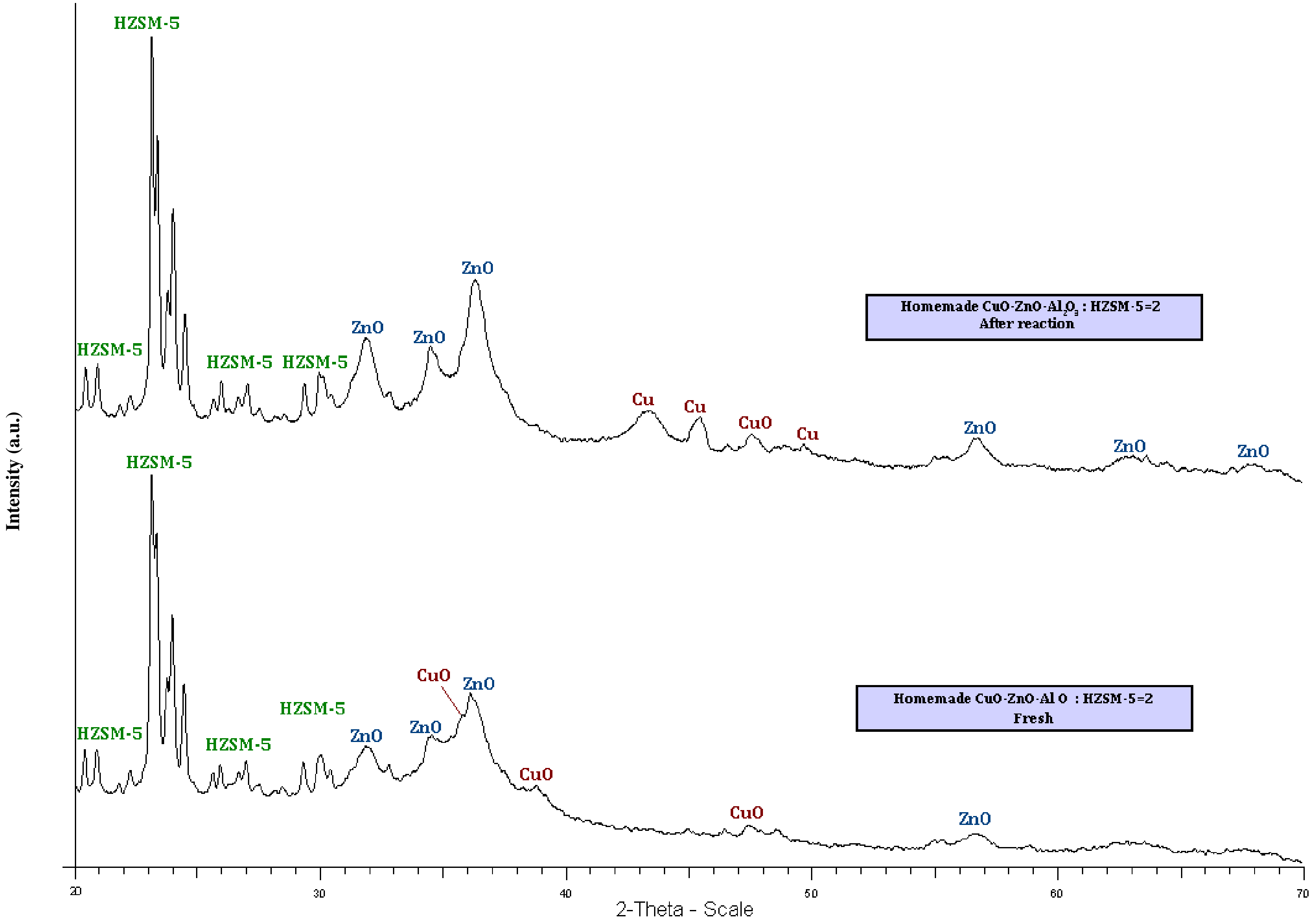

Figure 4-1: XRD results for CuO-ZnO-Al$_2$O$_3$: HZSM-5 =2 (fresh and after reaction)

4-2 Comparison of different catalyst ratios

4-2-1 The effect of GHSV

Fig. 4-2&4-3 show the effect of gas hourly space velocity (GHSV) on CO conversion and DME yield.

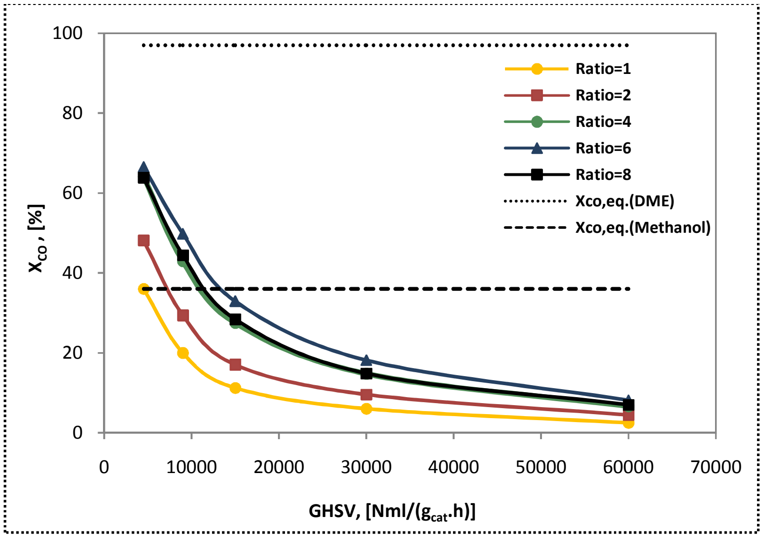

Figure 4-2: Effect of gas hourly space velocity (GHSV) on CO conversion.(Conditions: Fixed-bed reactor, 255 °C, 50 bar and H_2:CO = 2)

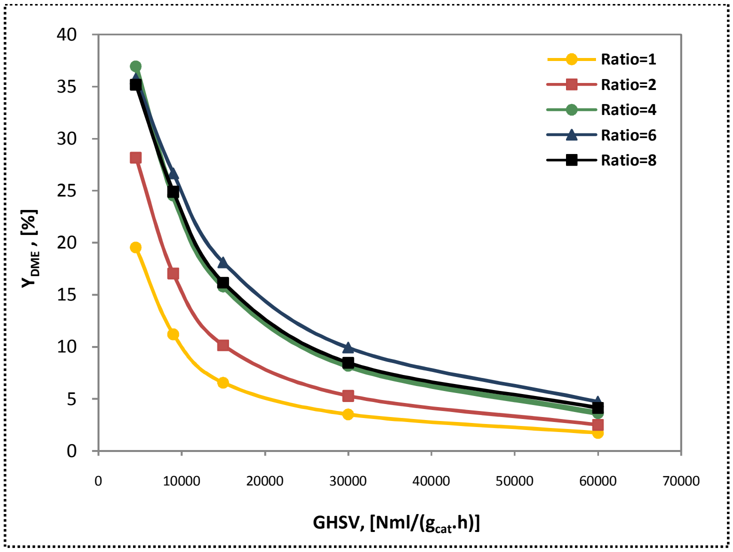

Figure 4-3: Effect of gas hourly space velocity (GHSV) on DME yield. (Conditions: Fixed-bed reactor, 255 °C, 50 bar and H_2:CO = 2)

It is obvious that CO conversion and DME yield are decreased with the increase of the gas GHSV for the different $\mathrm{CuO/ZnO/Al_2O_3}$ to $\mathrm{HZSM-5}$ mass ratios. With the increase of GHSV, the residence time becomes shortened, and thus CO conversion and DME yield are decreased. The bifunctional catalyst with mass ratio of 6 shows the better performance. The relatively large surface area of the HZSM-5 catalyst provides proper utilization of methanol produced by methanol synthesis catalyst (MSC) for the ratios up to 6.

The catalyst with mass ratio of 8 is going to be under methanol synthesis equilibrium limitation because methanol synthesis catalyst (MDC) is not enough to convert the methanol synthesized by MSC and will be affected by methanol synthesis equilibrium limitation.

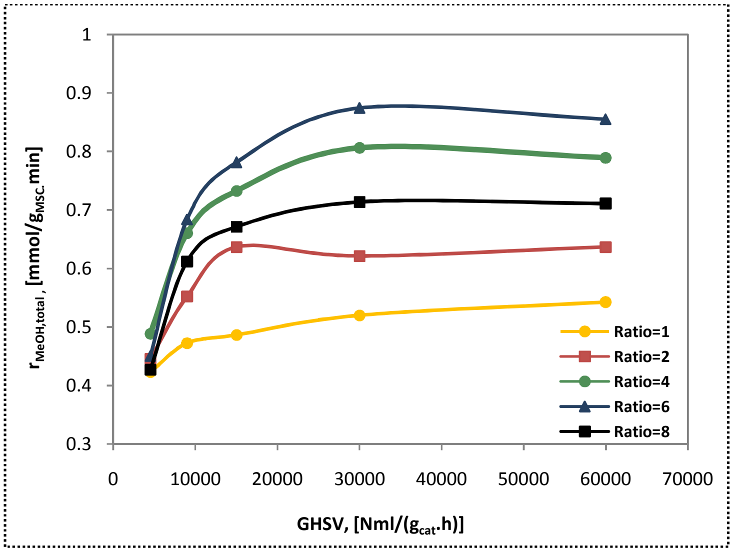

Figure 4-4: Effect of gas hourly space velocity (GHSV) on the rate of total methanol formation. (Conditions: Fixed-bed reactor, 255 °C, 50 bar, H_2:CO = 2 and the rate of total methanol formation is calculated based on the amount of methanol synthesis catalyst (MSC))

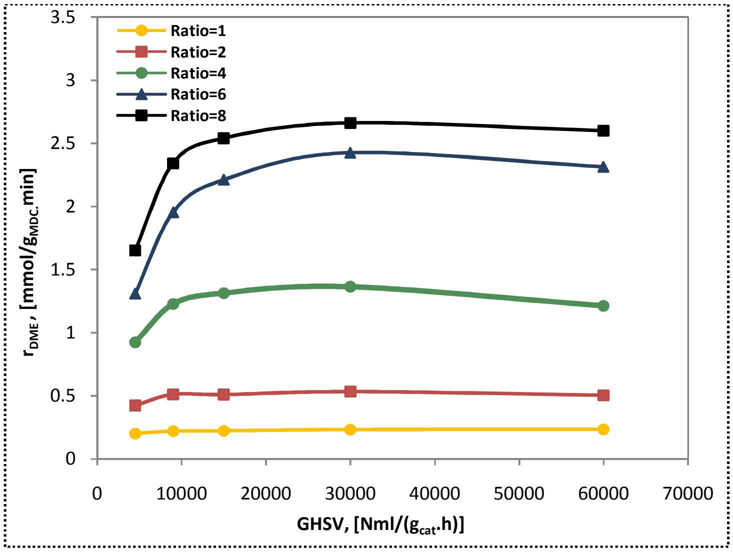

Figure 4-5: Effect of gas hourly space velocity (GHSV) on the rate of DME formation. (Conditions: Fixed-bed reactor, 255 °C, 50 bar, H_2:CO = 2 and the rate of DME formation is calculated based on the amount of methanol dehydration catalyst (MDC)).

As Fig.4-4&4-5 show, the rate of total methanol formation ($r_{MeOH,total}$) and DME formation (r_{DME}) increase by increasing $\mathrm{CuO/ZnO/Al_2O_3}$ to $\mathrm{HZSM-5}$ mass ratio for different GHSVs (except $r_{MeOH,total}$ for the catalyst with mass ratio of 8). Fig.4-5 demonstrates that r_{DME}, based on the amount of MDC used, increases with GHSV for the catalysts with mass ratios of 4, 6&8, and the lower GHSVs (4500-30000 Nml/(g_{cat}.h)), while for the higher GHSVs, r_{DME} slightly decreases. Increase in GHSV (for low GHSVs) enhances $r_{MeOH,total}$ that increases r_{DME}. The shorter residence time at higher GHSVs suppresses further reaction to form DME. At higher $r_{MeOH,total}$ larger amount of water produced by methanol synthesis reaction, possibly suppresses DME synthesis reaction, too. The catalysts with mass ratios of 1 and 2 give almost the same r_{DME} for all GHSVs. Existence of high enough MDC to utilize methanol produced by MSC, could be the reason.

At the higher GHSVs that reactions are far from DME synthesis equilibrium, $r_{MeOH,total}$ for the catalyst with mass ratio of 8 is less than that for the catalysts with ratios of 4 and 6. The lack of enough MDC to convert methanol produced by MSC could be the reason that makes the reactions under control of methanol synthesis equilibrium.

4-2-2 The effect of Temperature

Fig. 4-6&4-7 indicate that higher temperatures give faster kinetic and higher CO conversions and DME yields as long as DME synthesis equilibrium is not approached. The optimum temperatures could be exist. As Fig.4-6 shows, it is clear that the CO conversion exceeds methanol synthesis equilibrium limitation.

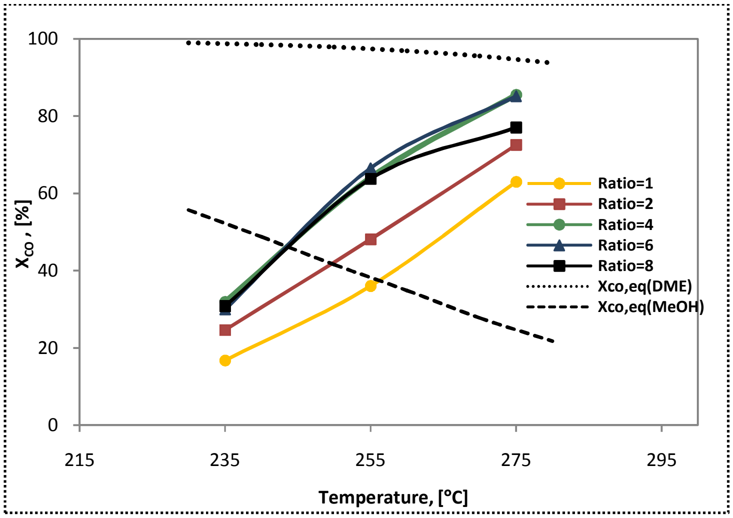

Figure 4-6: Effect of reaction temperature on CO conversion. (Conditions: Fixed-bed reactor, 50 bar, H_2:CO = 2 and GHSV = 4500 Nml/(g_{cat}.hr))

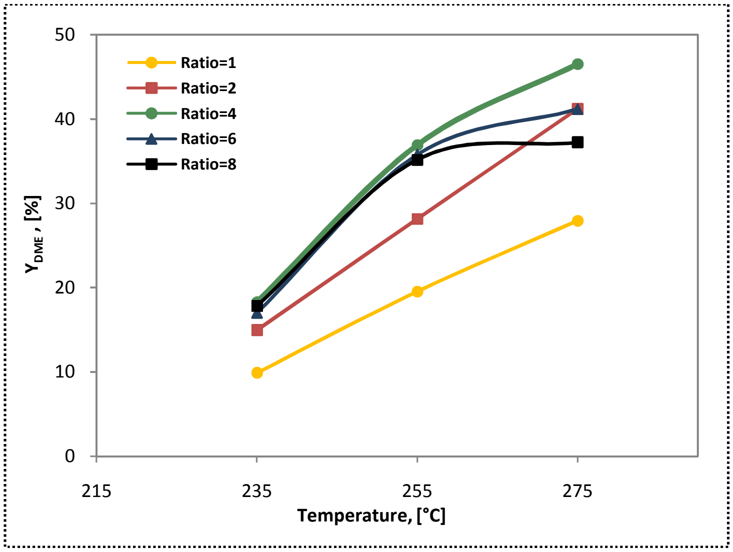

Figure 4-7: Effect of reaction temperature on DME yield. (Conditions: Fixed-bed reactor, 50 bar, H_2:CO = 2 and GHSV = 4500 Nml/(g_{cat}.hr))

The bifunctional catalysts with mass ratios of 4, 6 and 8 show the same DME yields at temperature range of 235-255°C. But for the higher temperatures, as the catalyst with mass ratio of 6 that has less MDC, with the same CO conversion compare to the catalyst with mass ratio of 4 gives less DME yield because the reaction is approaching DME synthesis equilibrium and its limitation lowers the DME yield. The catalyst with mass ratios of 4 shows better performance for all temperatures among the all ratios.

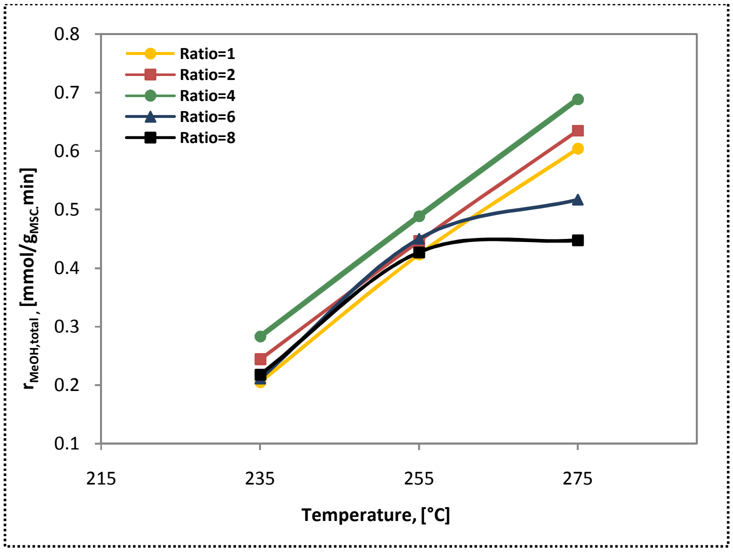

Figure 4-8: Effect of reaction temperature on the rate of total methanol formation. (Conditions: Fixed-bed reactor, 50 bar, H_2:CO = 2, GHSV = 4500 Nml/(g_{cat}.hr) and the rate of total methanol formation is calculated based on the amount of methanol synthesis catalyst (MSC))

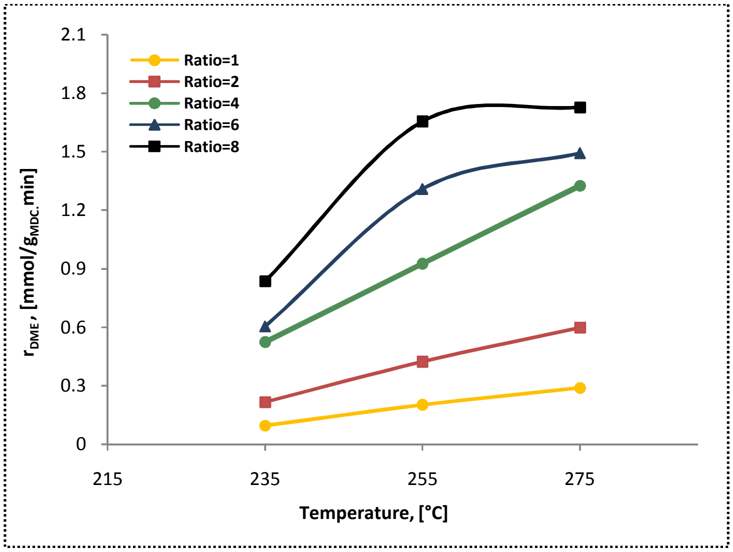

Figure 4-9: Effect of reaction temperature on the rate of DME formation. (Conditions: Fixed-bed reactor, 50 bar, H_2:CO = 2 , GHSV = 4500 Nml/(g_{cat}.hr) and the rate of DME formation is calculated based on the amount of methanol dehydration catalyst (MDC)).

As temperature increases $r_{MeOH,total}$ and r_{DME} will increase for the all catalysts with different mass ratios that are shown in the Fig.4-8&4-9. The catalyst mixture with the mass ratio of 4 shows the highest $r_{MeOH,total}$. At the higher temperatures the DME synthesis equilibrium limitation makes the reaction of methanol dehydration inverse and more methanol will be present, thus for catalysts with higher ratios can go under control of methanol synthesis equilibrium limitation.

At the low temperatures that reactions are far from equilibrium limitations, the $r_{MeOH,total}$, based on MSC, should be the same for all the catalysts that almost is the same except for the catalyst with ratio of 4. This area is controlled by kinetics. Possible small experimental errors can also be a reason for these difference.

4-2-3 The effect of H_2:CO feed ratio

The effect of H_2:CO feed ratio at constant CO_2 on CO conversion and DME yield are shown in Fig.4-10&4-11. As result shows, H_2-rich feeds give better CO conversion and DME yield. The reactions are not in the kinetic regime and they are affected by equilibrium limitations. The bifunctional catalyst with mass ratio of 6 shows higher CO conversion and by increasing the mass ratio, there will be no increase in CO conversion. The catalyst with mass ratio of 8 does not have enough MDC to convert the methanol synthesized by MSC and will be affected by methanol synthesis equilibrium limitation. High H_2:CO feed ratio influences water-gas-shift reaction and reverse water-gas-shift can occur, that could be the case for catalyst with ratio of 4 and at H_2-rich feeds. For the H_2:CO feed ratios of 1 and 2, the catalyst with mass ratio of 4 gives the highest DME yield and for the H_2-rich feeds, the catalyst with mass ratio of 6 shows better performance. The reverse water-gas-shift reaction can lowers the DME yield of the catalyst with mass ratio of 4. As it is producing H_2O and suppressing the methanol dehydration reaction.

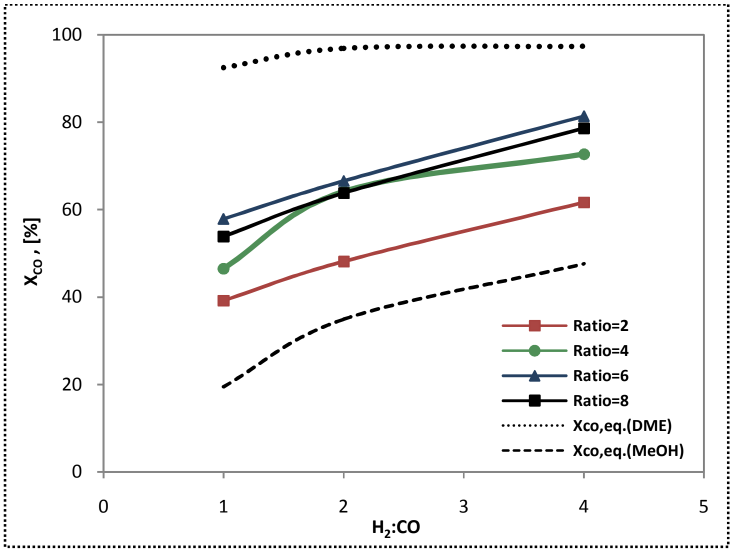

Figure 4-10: Effect of H_2:CO feed ratio on CO conversion. (Conditions: Fixed-bed reactor, 255 °C, 50 bar and GHSV = 4500 Nml/(g_{cat}.hr))

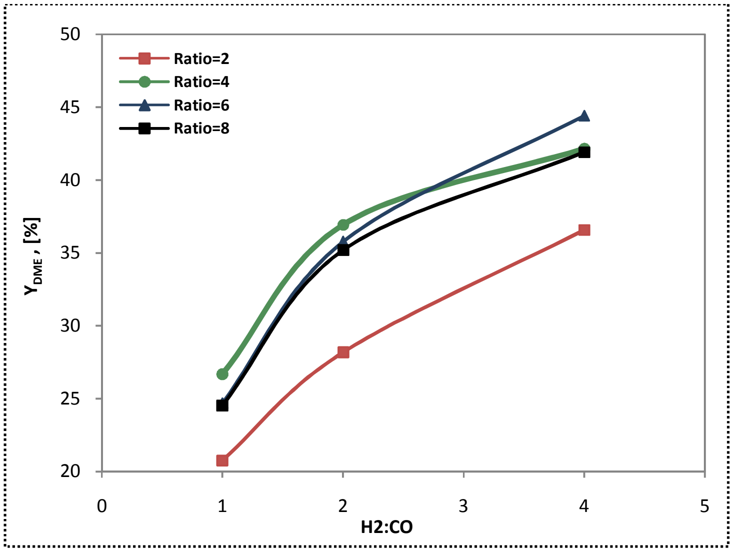

Figure 4-11: Effect of H_2:CO feed ratio on DME yield. (Conditions: Fixed-bed reactor, 255 °C, 50 bar and GHSV = 4500 Nml/(g_{cat}.hr))

According to Fig.4-11&12 by increasing the H_2:CO feed ratio $r_{MeOH,total}$ and r_{DME} will decrease for the all catalysts with different mass ratios. The catalyst with mass ratio of 8 does not have enough MDC to convert the methanol synthesized by MSC and will be affected by methanol synthesis equilibrium limitation. The catalyst with mass ratio of 4 gives the highest r_{DME} . The reactions affected by equilibrium limitations for the catalyst with higher ratios.

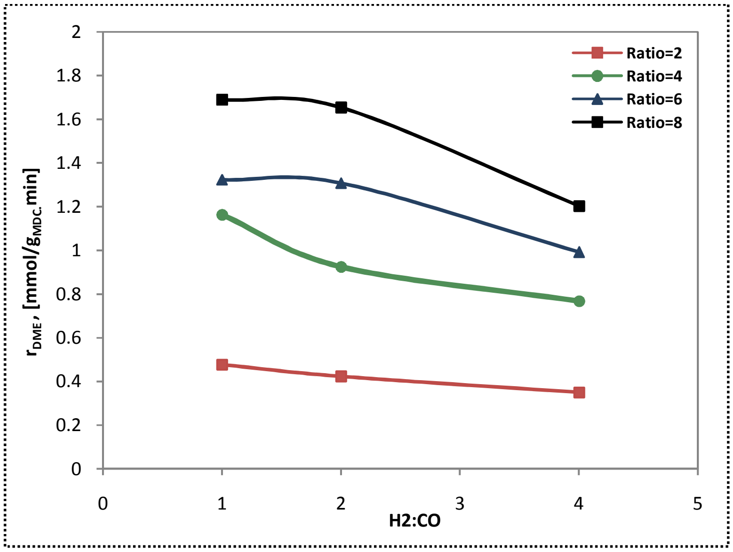

Figure 4-12: Effect of H_2:CO feed ratio on the rate of DME formation. (Conditions: Fixed-bed reactor, 255 °C, 50 bar, GHSV = 4500 Nml/(g_{cat}.hr) and the rate of DME formation is calculated based on the amount of methanol dehydration catalyst (MDC)).

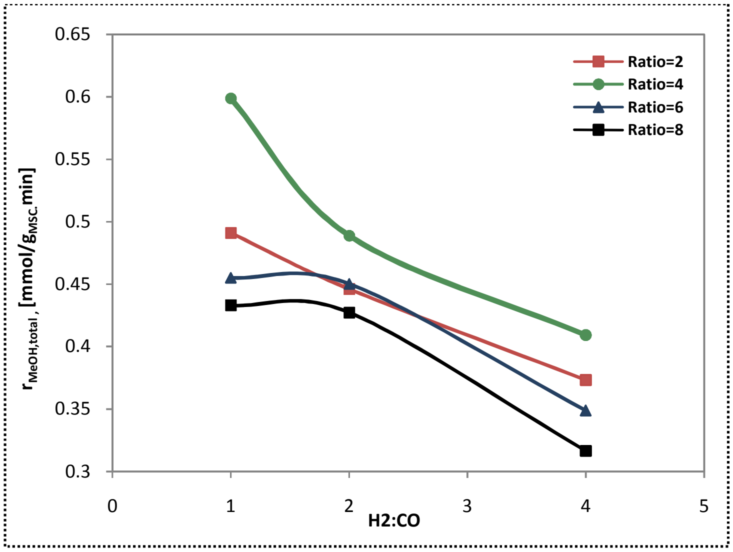

Figure 4-13: Effect of H_2:CO feed ratio on the rate of total methanol formation. (Conditions: Fixed-bed reactor, 255 °C, 50 bar, GHSV = 4500 Nml/(g_{cat}.hr) and the rate of total methanol formation is calculated based on the amount of methanol synthesis catalyst (MSC))

The bifunctional catalyst with mass ratio of 8 gives the lowest $r_{MeOH,total}$. According to the CO conversion result for this catalyst, methanol synthesis equilibrium is controlling the reaction. Also this is the case for catalyst with ratio of 6.

5 CONCLUSION AND FUTURE WORK

5.1 Conclusions

The effect of GHSV: The bifunctional catalyst with mass ratio of 6 shows better performance for different GHSVs. The relatively large surface area of the HZSM-5 catalyst provides proper utilization of methanol produced by methanol synthesis catalyst (MSC) for the ratios up to 6. The catalyst with mass ratio of 8 is going to be under methanol synthesis equilibrium limitation because methanol synthesis catalyst (MDC) is not enough to convert the methanol synthesized by MSC and will be affected by methanol synthesis equilibrium limitation. The catalysts with mass ratios of 1 and 2 give almost the same rate of DME formation for all GHSVs. Existence of high enough MDC to utilize methanol produced by MSC, could be the reason.

The effect of temperature: The bifunctional catalysts with mass ratios of 4, 6 and 8 show the same DME yields at temperature range of 235-255°C. At the higher temperatures, the bifunctional catalysts with mass ratios of 4 and 6 show higher CO conversions and DME yields. At the higher temperatures the reaction is approaching DME synthesis equilibrium and its limitation lowers the conversion and DME yield. The catalyst with mass ratios of 4 shows better performance for all temperatures among the all ratios.

The effect of H_2:CO feed ratio: H_2-rich feeds give better CO conversion and DME yield. The bifunctional catalyst with mass ratio of 6 shows higher CO conversion and by increasing the mass ratio, there will be no increase in CO conversion. High H_2:CO feed ratio influences water-gas-shift reaction and reverse water-gas-shift can occur, that could be the case for catalyst with ratio of 4. For the H_2:CO feed ratios of 1 and 2, the catalyst with mass ratio of 4 gives the highest DME yield and for the H_2-rich feeds, the catalyst with mass ratio of 6 shows better performance. As the reverse water-gas-shift is producing H_2O and suppresses the methanol dehydration reaction. According to the results by increasing the H_2:CO feed ratio, the rate of methanol and DME formation will decrease for the all catalysts with different mass ratios. The catalyst with mass ratio of 4 gives the highest rate of DME. The reactions affected by equilibrium limitations for the catalyst with higher ratios.

And finally,

According to the results the optimum $\mathrm{CuO/ZnO/Al_2O_3}$ to $\mathrm{HZSM-5}$ mass ratio could be between 4-6.

5.2 Future works

Future work can be:

- Synthesis of new catalyst by good catalyst preparation methods that give synergetic effect to the catalyst mixture.
- Examine of suitable additives.
- Study of different and newly synthesized zeolites for the indirect process and then test in the direct process.

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APPENDICES

A REACTION MECHANISMS

A.1 Methanol dehydration mechanism

The proposed reaction mechanism by S.J. Royaee et al. (39) is as follows:

$$M_{(g)} + S \leftrightarrow M.S^{*} \tag{A-1}$$

$$M.S^{*} + mM \leftrightarrow M_{m}(M.S) \tag{A-2}$$

$$M.S^{*} + nW \leftrightarrow W_{n}(M.S) \tag{A-3}$$

$$W + S \leftrightarrow WS \tag{A-4}$$

$$2M.S^{*} \leftrightarrow D_{(g)} + WS + S \tag{A-5}$$

Where:

$M_{(g)}$: MeOH in gas phase

$M.S^{*}$: An active intermediate involving bonding between the unique zeolite surface species and adsorbed MeOH

$M_{m}(M.S)$ and $W_{n}(M.S)$: ‘inactive’ intermediate species (m and n are integer number equal or larger than 1)

W : Water

$D_{(g)}$: DME in the gas phase

WS : Adsorbed water on free catalyst acidic sites

Considering reaction (A-5) (which leads to the release of the chemisorbed DME from the acidic sites to the gas phase) as the controlling step, the resulting rate equation may be derived as follows:

$$-r_{M} = \frac{K_{r}K_{M}{}^{2}P_{M}{}^{2} - K_{r}{}'K_{W}P_{D}P_{W}}{\left(1+K_{M}P_{M}+K_{W}P_{W}+K_{N}K_{M}P_{M}{}^{m+1}+K_{NN}K_{M}P_{M}P_{W}{}^{n}\right)^{2}} \tag{A-6}$$

Where: K_{r} and $K_{r}{}'$: The forward and backward reaction rate constants of reaction (A-5)

K_{M} : The adsorption equilibrium constant of reaction (A-1)

K_{N} : The adsorption equilibrium constant of reaction (A-2)

K_{W} : The adsorption equilibrium constant of reaction (A-4)

K_{NN} : The adsorption equilibrium constant of reaction (A-3)

P_{D} : The partial pressure of DME (atm)

P_{W} : The partial pressure of water (atm)

P_{M} : The partial pressure of MeOH (atm)

Eq. (A-6) may be simplified to the following final form:

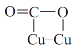
$$-r_M = \frac{K_r K_M{}^2 P_M{}^2}{\left(1+K_M P_M + K_N K_M P_M{}^4 + K_{NN} K_M P_M P_W\right)^2} \qquad \text{(A-7)}$$

A.2 Synthesis gas to DME mechanism

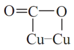
The proposed reaction mechanism (based on Cu–ZnO–Al_2O_3/HZSM-5 and CO_2 hydrogenation to methanol and water gas shift reaction) by W.Zh. Lu et al. (11) is as follows:

$$2Cu_2 + H_2 \leftrightarrow 2Cu_2H \qquad \text{(A-8)}$$

$$Co_2 + Cu_2 \leftrightarrow$$



$$\begin{matrix} O{=}C{-}O \\ |\qquad | \\ Cu{-}Cu \end{matrix} \qquad \text{(A-9)}$$



$$\begin{matrix} O{=}C{-}O \\ |\qquad | \\ Cu{-}Cu \end{matrix} + 2Cu_2H \leftrightarrow 2Cu_2CH_2O + Cu_2O + Cu_2 \qquad \text{(A-10)}$$

$$Cu_2CH_2O + Cu_2H \leftrightarrow Cu_2CH_3O + Cu_2 \qquad \text{(A-11)}$$

$$Cu_2CH_3O + Cu_2H \leftrightarrow Cu_2CH_3OH + Cu_2 \qquad \text{(A-12)}$$

$$Cu_2CH_3OH \leftrightarrow CH_3OH(a) + Cu_2 \qquad \text{(A-13)}$$

$$Cu_2O + 2Cu_2H \leftrightarrow 2Cu_2 + Cu_2H_2O \qquad \text{(A-14)}$$

$$Cu_2H_2O \leftrightarrow Cu_2 + H_2O(a) \qquad \text{(A-15)}$$

$$H_2O(a) + Cu_2 \leftrightarrow Cu_2O + H_2 \qquad \text{(A-16)}$$

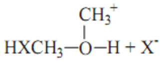
$$CO + Cu_2O \leftrightarrow Cu_2 + CO_2 \qquad \text{(A-17)}$$

Reaction (A-10) and (A-16) are assumed to be the rate determining steps individually. The reaction mechanism for the formation of DME is as follows:

$$CH_3OH(a) + HX \leftrightarrow HXCH_3OH \qquad \text{(A-18)}$$

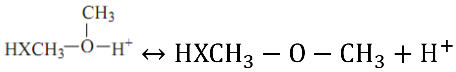
$$HXCH_3OH \leftrightarrow CH_3{}^+X^- + H_2O(a) \qquad \text{(A-19)}$$

$$CH_3{}^+X^- + HXCH_3OH \leftrightarrow$$



$$HXCH_3{-}\overset{\overset{\large CH_3{}^+}{|}}{O}{-}H + X^- \qquad \text{(A-20)}$$

$$HXCH_3-\overset{CH_3^+}{\overset{|}{O}}-H \rightleftharpoons HXCH_3-\overset{CH_3}{\overset{|}{O}}-H^+ \qquad \text{(A-21)}$$



$$HXCH_3-\overset{CH_3}{\overset{|}{O}}-H^+ \leftrightarrow HXCH_3-O-CH_3+H^+ \qquad \text{(A-22)}$$

$$HXCH_3-O-CH_3 \leftrightarrow CH_3-O-CH_3+HX \qquad \text{(A-23)}$$

$$H^+ + X^- \leftrightarrow HX \qquad \text{(A-24)}$$

Here reaction (A-20) is assumed to be the rate determining step. Based on these kinetics one could obtain the following rate expressions:

$$r_2 = K_2\frac{\left(\frac{P_M{}^2}{P_W}-\frac{P_D}{K_{P,2}}\right)}{(1+K_M P_M+K_W P_W)^2} \qquad \text{(W: water , M: methanol)} \qquad \text{(A-25)}$$

The reaction rate for the methanol formation reaction is:

$$r_1 = K_1\frac{\left(P_{CO_2}P_{H_2}-\frac{P_W P_M}{K_{P,1}P_{H_2}{}^2}\right)}{\left(1+K_{CO_2}P_{CO_2}+K_{CO}P_{CO}+\sqrt{K_{H_2}P_{H_2}}\right)^3} \qquad \text{(W: water , M: methanol)} \qquad \text{(A-26)}$$

The reaction rate for the methanol dehydration reaction is:

$$r_2 = K_2\left(\frac{P_M{}^2}{P_W}-\frac{P_D}{K_{P,2}}\right) \qquad \text{(D: DME)} \qquad \text{(A-27)}$$

The reaction rate for the water gas shift reaction is:

$$r_3 = K_3\frac{\left(P_W-\frac{P_{CO_2}P_{H_2}}{K_{P,3}P_{CO}}\right)}{\left(1+K_{CO_2}P_{CO_2}+K_{CO}P_{CO}+\sqrt{K_{H_2}P_{H_2}}\right)} \qquad \text{(A-28)}$$

The constants K_1, K_2, K_3 (kinetic parameters), K_{CO2}, K_{CO}, K_{H2} (adsorption constants), $K_{P,1}$, $K_{P,2}$ and $K_{P,3}$ (equilibrium constants) are defined as:

$$K_1 = 35.45\exp\left(\frac{-1.7069\times10^4}{RT}\right)$$

$$K_2 = 8.2894\times10^4\exp\left(\frac{-5.294\times10^4}{RT}\right)$$

$$K_3 = 7.3976\exp\left(\frac{-2.0436\times10^4}{RT}\right)$$

$$K_{H_2} = 0.249\exp\left(\frac{-3.4394\times10^4}{RT}\right)$$

$$K_{CO_2} = 1.02 \times 10^{-7} \exp\left(\frac{6.74 \times 10^4}{RT}\right)$$

$$K_{CO} = 7.99 \times 10^{-7} \exp\left(\frac{5.81 \times 10^4}{RT}\right)$$

$$\ln K_{P,1} = \frac{4213}{T} - 5.752 \ln T - 1.707 \times 10^{-3} T + 2.682 \times 10^{-6} T^2 - 7.232 \times 10^{-10} T^3 - 26.64$$

$$\ln K_{P,2} = \frac{4019}{T} + 3.707 \ln T - 2.783 \times 10^{-3} T + 3.8 \times 10^{-7} T^2 - \frac{6.651 \times 10^4}{T^3} - 26.64$$

$$\ln K_{P,3} = \frac{2167}{T} - 0.5194 \ln T - 1.037 \times 10^{-3} T - 2.331 \times 10^{-7} T^2 - 1.2777$$

B GC PROCEDURE

The procedure for the GC operation could be as following steps:

STEP 1

Set the gas source pressures and check for leaks. GC needs 3 chromatographic- grade gases. These gases are: helium as carrier gas, hydrogen and air. Table D-1 shows the recommended and maximum pressures of the gases.

Table B-1: Recommended and maximum gas pressures for the GC

Gas	Recommended	Maximum
Helium	4 bar	6,9 bar
Hydrogen	4 bar	6,9 bar
Air	5,5 bar	6,9 bar

STEP 2

Set the gaseous product pressure to the GC according to the following steps:

- Press **[Time]** (Fig. D-1)
- Set the pressure of gaseous product to the GC (Fig. D-2) that has to be about 1 bar.
- Inject a little water to the bubble flow meter and generate a bubble (Fig. D-4). When it passed the first line in the bubble flow meter, press **[Enter]** and wait until the bubble passes the second line to press **[Enter]** again.
    - If 1/t is not between 20 and 35 (Fig D-3), press **[Clear],** change the pressure and repeat step 3.

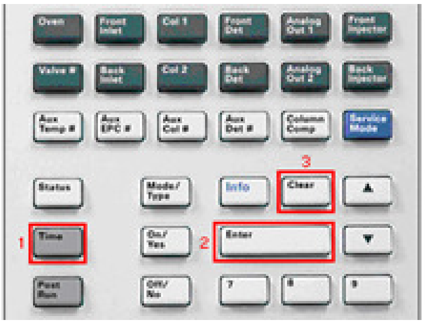


Figure B-1: Keypad for the 7890A GC

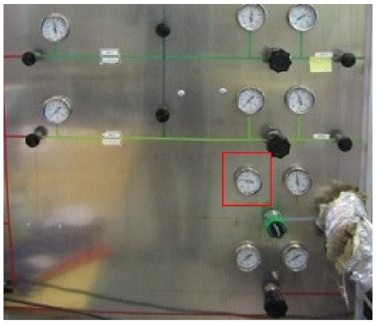


Figure B-2: The pressure of the gaseous product

```
8:13:28  Thu 24 Jun 2010
Elapsed time        6.092
Time left           3.908
time =  0:00.0  1/t =  0.000<
```

Figure B-3: GC monitor

Figure B-4: GC and the bubble flow meter

STEP 3

Use the software (**Agilent ChemStation**) to run the GC automatically. The following figures show how we can run the GC by **Agilent ChemStation:**

- Open *Instrument 1*(online) (Fig D-5)
- Select the *Sequence parameter* in *Sequence* menu and define the *Subdirectory* (Fig D-6&7)
- Select the *Sequence table* in *Sequence* menu and define the *Method* (Fig D-8&9)
- Select the *Run sequence* in *Run control* menu to start the run (Fig D-10)

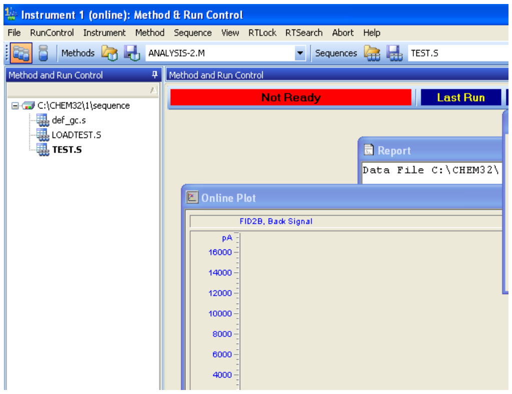


Figure B-5: Agilent ChemStation – Before Run

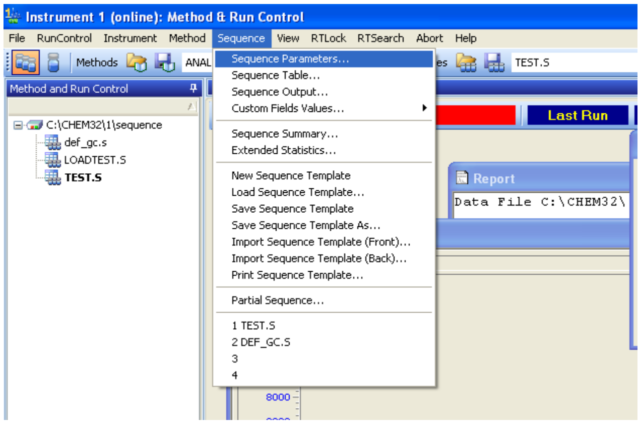
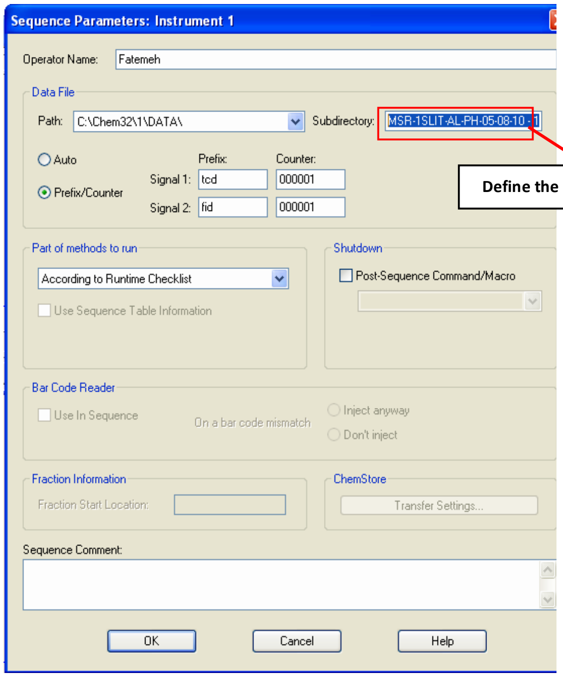


Figure B-6: Agilent ChemStation –Sequence Parameters



Operator Name: Fatemeh

Path: C:\Chem32\1\DATA\

Subdirectory: MSR-1SLIT-AL-PH-05-08-10 - 1

○ Auto

● Prefix/Counter

Signal 1: Prefix: tcd Counter: 000001

Signal 2: Prefix: fid Counter: 000001

According to Runtime Checklist

☐ Use Sequence Table Information

☐ Post-Sequence Command/Macro

☐ Use In Sequence

On a bar code mismatch ○ Inject anyway ○ Don't inject

Fraction Start Location:

Sequence Comment:

Define the subdirectory

Figure B-7: Agilent ChemStation – Definition of Subdirectory

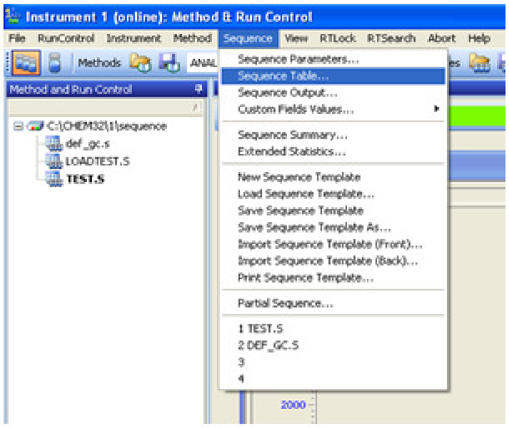
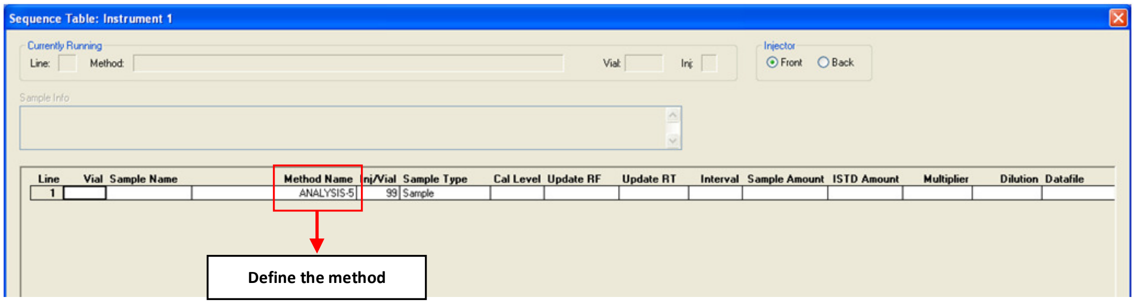


Figure B-8: Agilent ChemStation –Sequence Table



Line	Vial	Sample Name	Method Name	Inj/Vial	Sample Type	Cal Level	Update RF	Update RT	Interval	Sample Amount	ISTD Amount	Multiplier	Dilution	Datafile
1			ANALYSIS-5	99	Sample									

Define the method

Figure B-9: Agilent ChemStation – Definition of Method

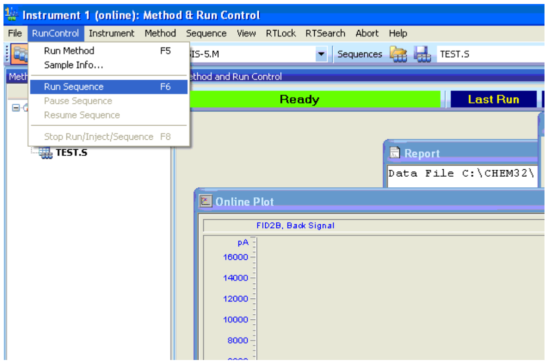


Figure B-10: Agilent ChemStation – Run Sequence

C FLOW CONTROLLER

The following figures show the procedure for using the flow controller.

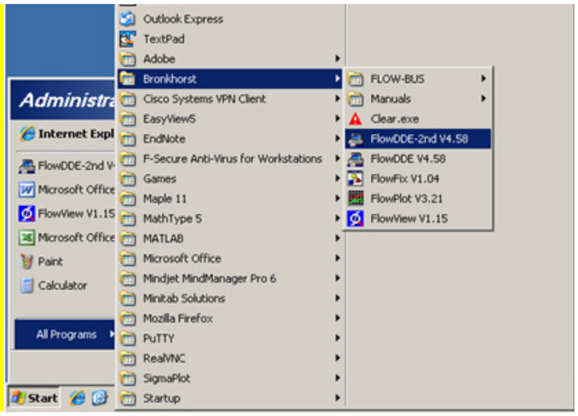
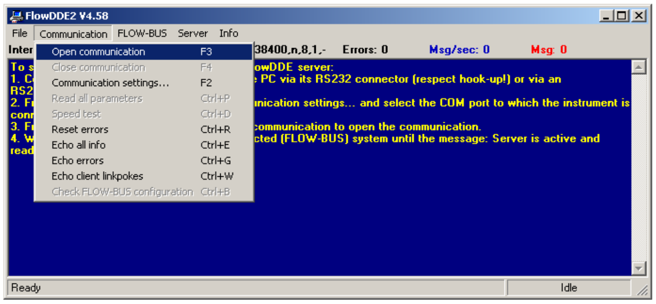
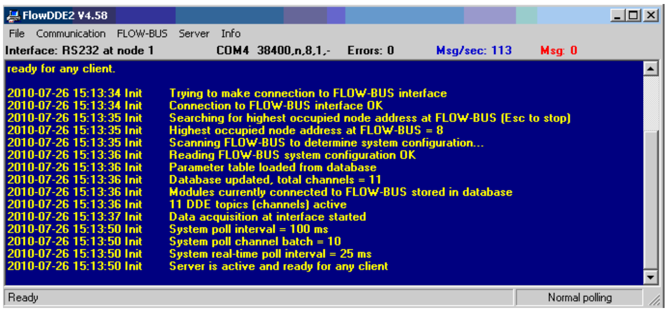


Figure C-1: FlowDDE-2nd V4.58



```
Inter                    38400,n,8,1,-    Errors: 0     Msg/sec: 0     Msg: 0
To s                     owDDE server:
1. C                     : PC via its RS232 connector (respect hook-up!) or via an
RS2
2. F                     inication settings... and select the COM port to which the instrument is
conr
3. F                     communication to open the communication.
4. W                     cted (FLOW-BUS) system until the message: Server is active and
read
```

Figure C-2: FlowDDE-2nd V4.58 – Open communication



```
Interface: RS232 at node 1          COM4  38400,n,8,1,-    Errors: 0     Msg/sec: 113     Msg: 0
ready for any client.

2010-07-26 15:13:34 Init      Trying to make connection to FLOW-BUS interface
2010-07-26 15:13:34 Init      Connection to FLOW-BUS interface OK
2010-07-26 15:13:35 Init      Searching for highest occupied node address at FLOW-BUS (Esc to stop)
2010-07-26 15:13:35 Init      Highest occupied node address at FLOW-BUS = 8
2010-07-26 15:13:35 Init      Scanning FLOW-BUS to determine system configuration...
2010-07-26 15:13:36 Init      Reading FLOW-BUS system configuration OK
2010-07-26 15:13:36 Init      Parameter table loaded from database
2010-07-26 15:13:36 Init      Database updated, total channels = 11
2010-07-26 15:13:36 Init      Modules currently connected to FLOW-BUS stored in database
2010-07-26 15:13:36 Init      11 DDE topics (channels) active
2010-07-26 15:13:37 Init      Data acquisition at interface started
2010-07-26 15:13:50 Init      System poll interval = 100 ms
2010-07-26 15:13:50 Init      System poll channel batch = 10
2010-07-26 15:13:50 Init      System real-time poll interval = 25 ms
2010-07-26 15:13:50 Init      Server is active and ready for any client
```

Figure C-3: FlowDDE-2nd V4.58 – Ready for any client

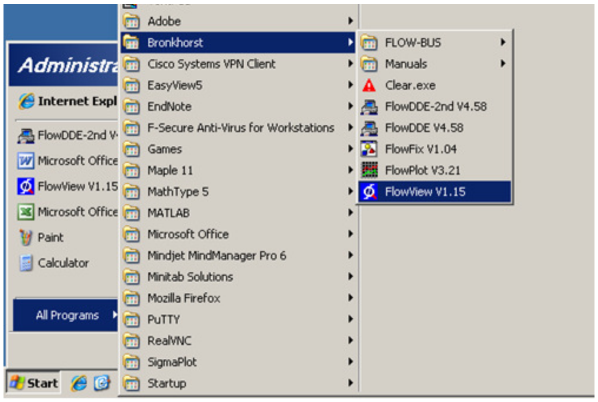


Figure C-4: Flow View V1.15

D EUROTHERM MODEL 2416

The fixed-bed reactor is clamped inside an aluminum block and heated by a Kanthal oven. The temperature is controlled by an Eurotherm model 2416.

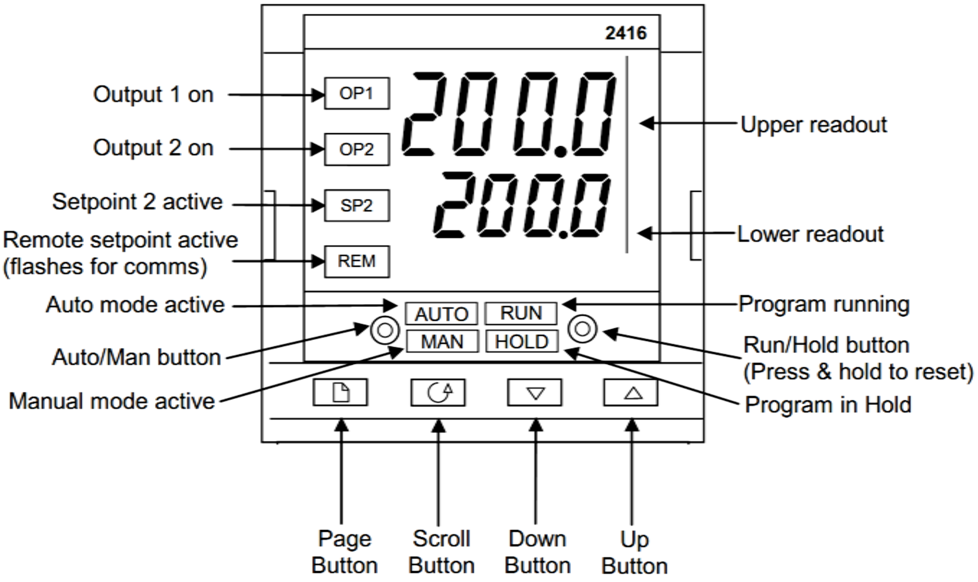


Figure D-1: Front panel layout

D.1 Basic operation

Switch on the power to the controller. It runs through a self-test sequence for about three seconds and then shows the temperature, or process value, in the upper readout and the setpoint in the lower readout. This is called the Home display. It is the one that you will use most often.

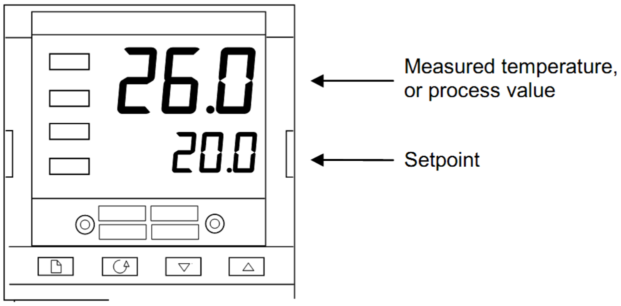


Figure D-2: Home display

On this display you can adjust the setpoint by pressing the ▲ or ▼ buttons. Two seconds after releasing either button, the display blinks to show that the controller has accepted the new value.

Note: You can get back to the Home display at any time by pressing ⟳ and 🗋 together. Alternatively you will always be returned to the Home display if no button is pressed for 45 seconds, or whenever the power is turned on. If, however, a flashing alarm message is present the controller reverts to the Home display after 10 seconds.

Table D-1: Controller buttons and indicators

Button or indicator	Name		Explanation
OP1	Output 1	If a DC output is installed OP1 & OP2 will not light	When lit, it indicates that the output installed in module position 1 is on. This is normally the heating output on a temperature controller.
OP2	Output 2		When lit, it indicates that the output installed in module position 2 is on. This is normally the cooling output on a temperature controller.
SP2	Setpoint 2		When lit, this indicates that setpoint 2, (or a setpoint 3-16) has been selected.
REM	Remote setpoint		When lit, this indicates that a remote setpoint input has been selected. 'REM' will also flash when communications is active.
◎ AUTO MAN	Auto/Manual button		When pressed, this toggles between automatic and manual mode: • If the controller is in automatic mode the AUTO light will be lit. • If the controller is in manual mode, the MAN light will be lit. The Auto/Manual button can be disabled in configuration level.
RUN HOLD ◎	Run/Hold button		• Press once to start a program (RUN light on.) • Press again to hold a program (HOLD light on) • Press again to cancel hold and continue running (HOLD light off and RUN light ON) • Press and hold in for two seconds to reset a program (RUN and HOLD lights off) The RUN light will flash at the end of a program. The HOLD light will flash during holdback or when a PDS retransmission output is open circuit.
🗋	Page button		Press to select a new list of parameters.
⟳	Scroll button		Press to select a new parameter in a list.
▼	Down button		Press to decrease a value in the lower readout.
▲	Up button		Press to increase a value in lower readout.

D.2 Operating modes

The controller has two basic modes of operation:

- **Automatic mode** in which the output power is automatically adjusted to maintain the temperature or process value at the setpoint.
- **Manual mode** in which you can adjust the output power independently of the setpoint.

You toggle between the modes by pressing the AUTO/MAN button. Two other modes are also available:

- **Remote Setpoint mode** in which the setpoint is generated from an external source. In this mode the REM light will be on.
- **Programmer mode**

More information is available here:

http://www.etherm.cz/eurotherm_regulatory/teplotni_a_procesni_regulatory/2416/2416_man_en.pdf

E HIGH TEMPERATURE CIRCULATOR OIL

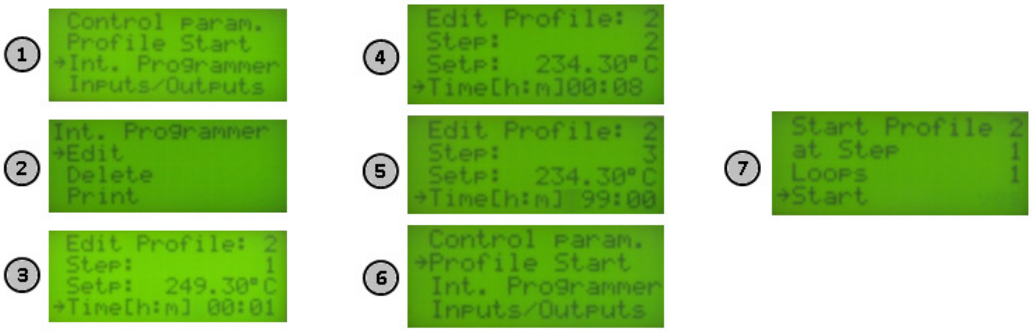
The microstructured reactor unit is heated by a *Julabo HT30-M1* High temperature circulator with working temperature $70-400^{\circ}\ C$ and Thermal H350 Heat Transfer Oil with working temperatures 50 °C to 350 °C.

Figure E-1: High temperature circulator oil

Example

Change the temperature from 250 °C to 235 °C

- ESC 2 times.
- Select **[Int. programmer]** ↵
- Select **[Edit]** ↵
- In the **[profile 2]**:
  - Go to **[step]** and enter **1** ↵ ⟶ in **[setp]** enter **249.3** ↵ ⟶ in **[time]** enter **00:01** ↵
  - Go to **[step]** and enter **2** ↵ ⟶ in **[setp]** enter **234.3** ↵ ⟶ in **[time]** enter **00:08** ↵
  - Go to **[step]** and enter **3** ↵ ⟶ in **[setp]** enter **234.3** ↵ ⟶ in **[time]** enter **99:00** ↵
- ESC 2 times.
- Select **[Start profile]** ↵
- In the **[profile 2]**: at **[step 1]** ⟶ **[Loops 1]** ⟶ in **[Start** P→ (to change **No** to **Yes**) ↵ .



①
```
 Control param.
 Profile Start
→Int. Programmer
 Inputs/Outputs
```

②
```
Int. Programmer
→Edit
 Delete
 Print
```

③
```
 Edit Profile: 2
 Step:          1
 Setp:   249.30°C
→Time[h:m] 00:01
```

④
```
 Edit Profile: 2
 Step:          2
 Setp:   234.30°C
→Time[h:m]00:08
```

⑤
```
 Edit Profile: 2
 Step:          3
 Setp:   234.30°C
→Time[h:m] 99:00
```

⑥
```
 Control param.
→Profile Start
 Int. Programmer
 Inputs/Outputs
```

⑦
```
 Start Profile 2
 at Step       1
 Loops         1
→Start
```

Figure E-2: Change the temperature from 250 °C to 235 °C

F ADDITIONAL N_2 PHYSISORPTION RESULTS

F.1 Isotherm linear plots

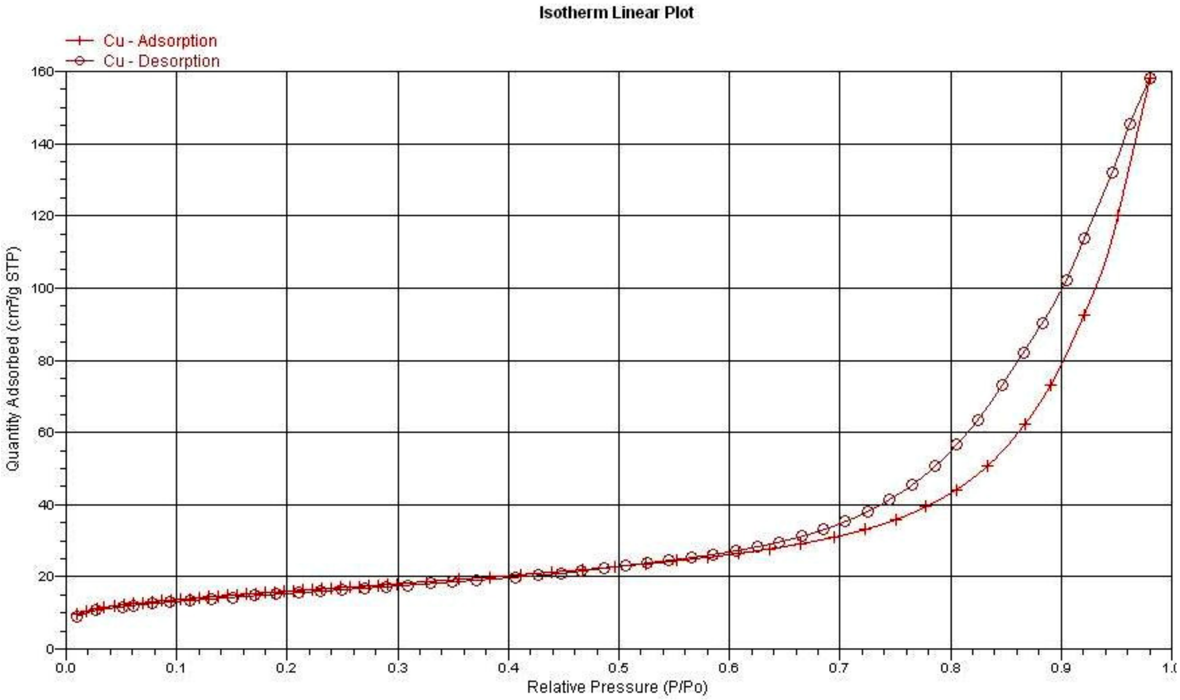


Figure F-1: Isotherm linear plot for CuO-ZnO-Al_2O_3

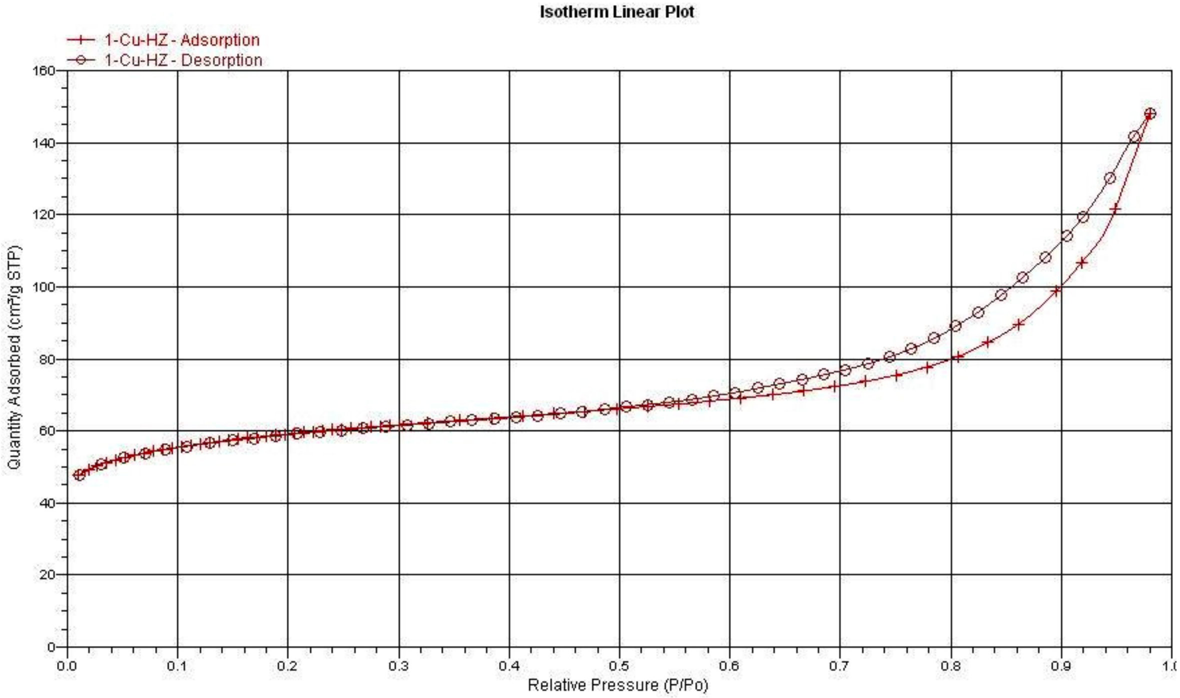


Figure F-2: Isotherm linear plot for CuO-ZnO-Al_2O_3 : HZSM-5=1

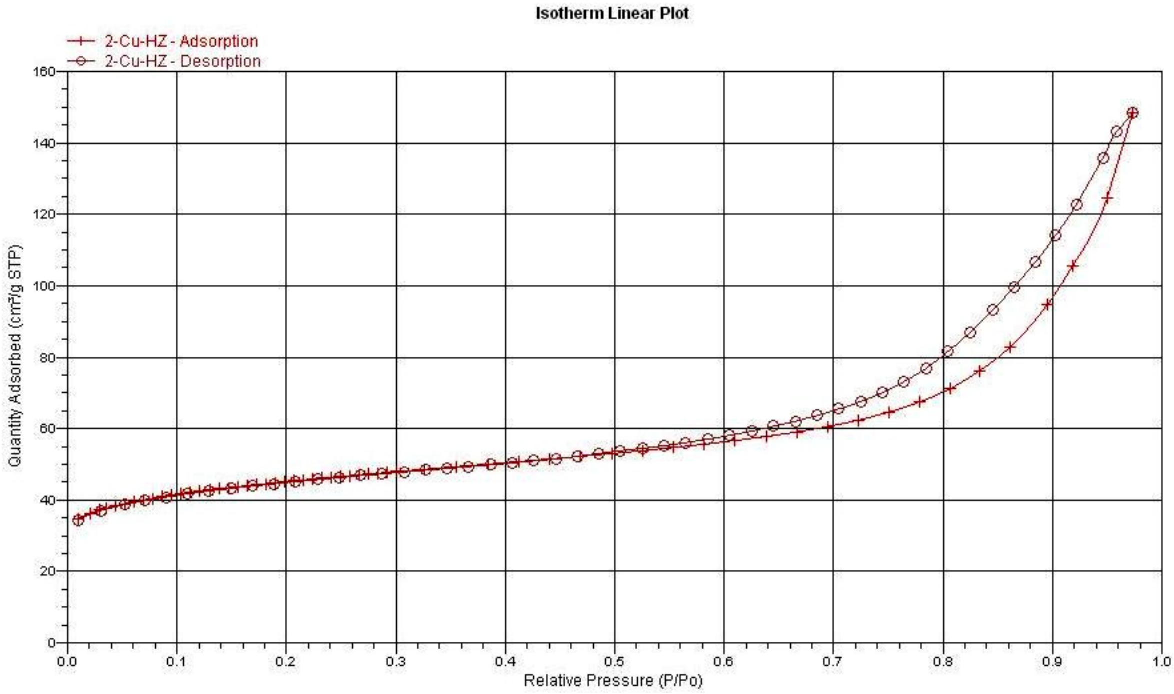


Figure F-3: Isotherm linear plot for CuO-ZnO-Al_2O_3 : HZSM-5=2

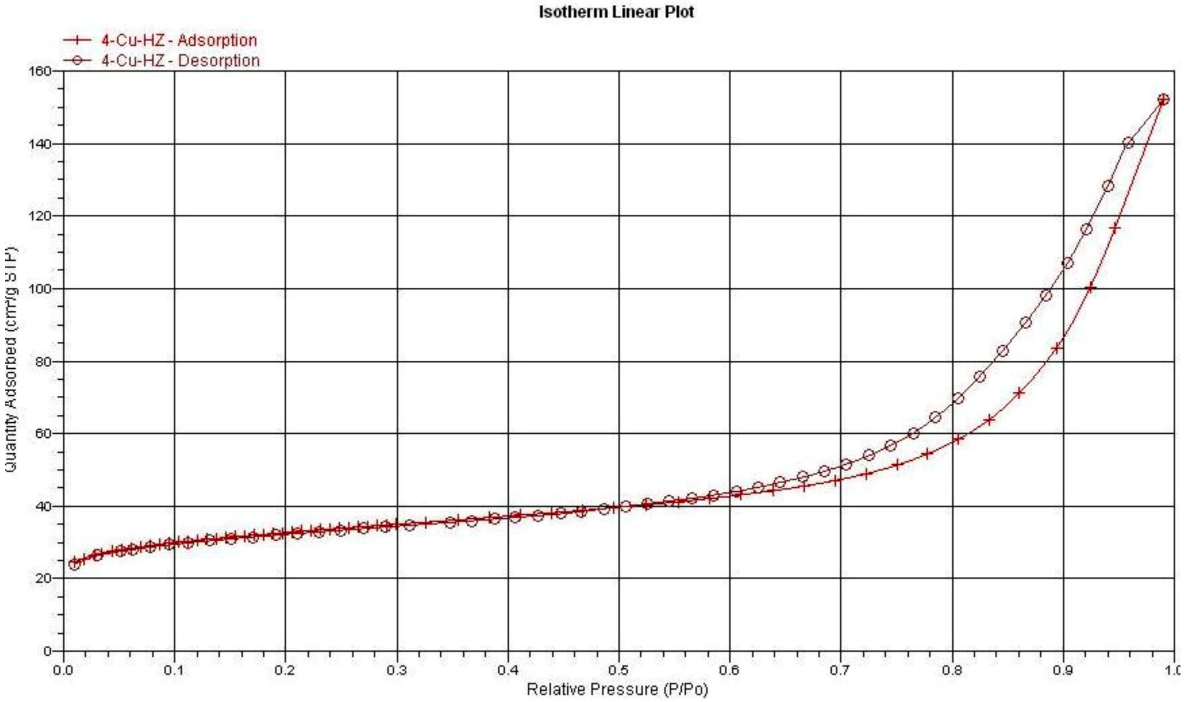


Figure F-4: Isotherm linear plot for CuO-ZnO-Al_2O_3 : HZSM-5=4

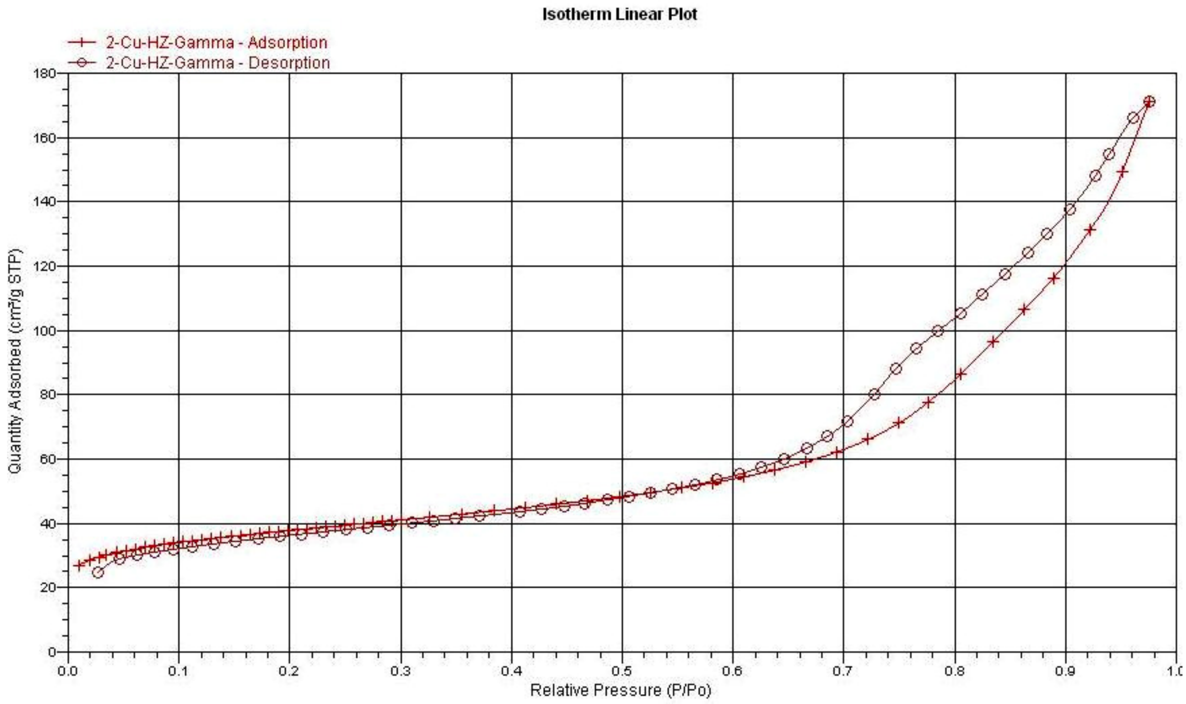


Figure F-5: Isotherm linear plot for CuO-ZnO-Al_2O_3 : (50%HZSM-5+50%γ- Al_2O_3)=2

F.2 BET surface area plots

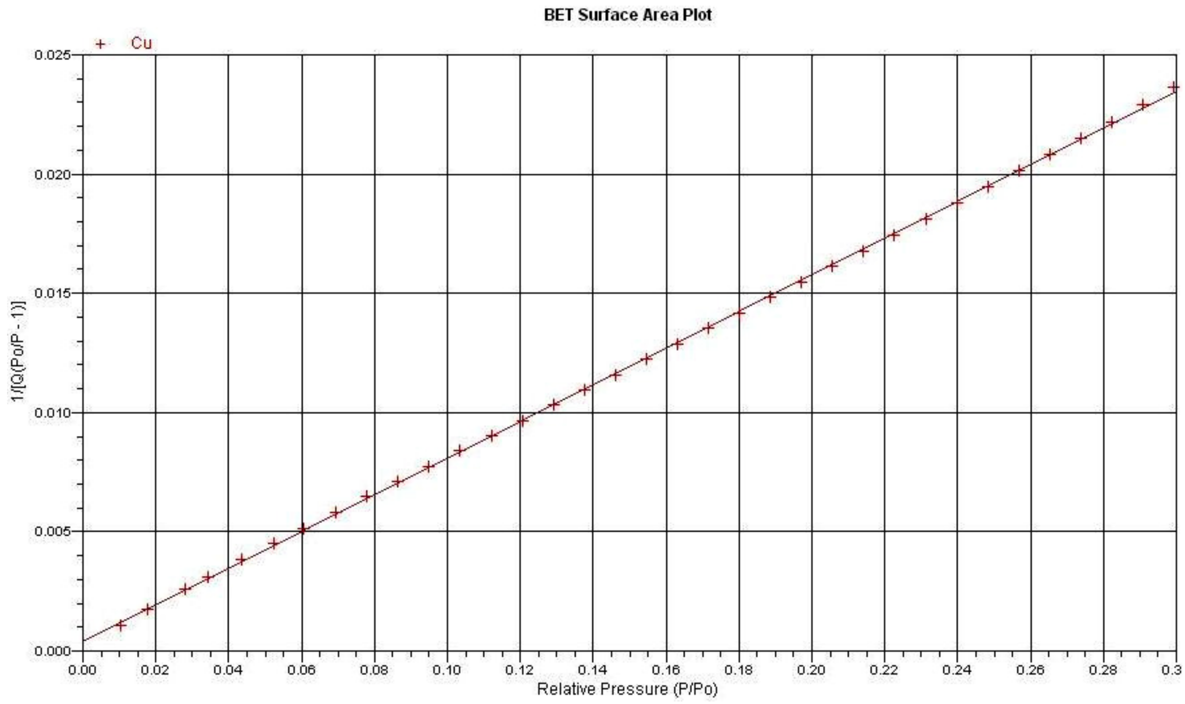


Figure F-6: BET surface area plot for CuO-ZnO-Al_2O_3

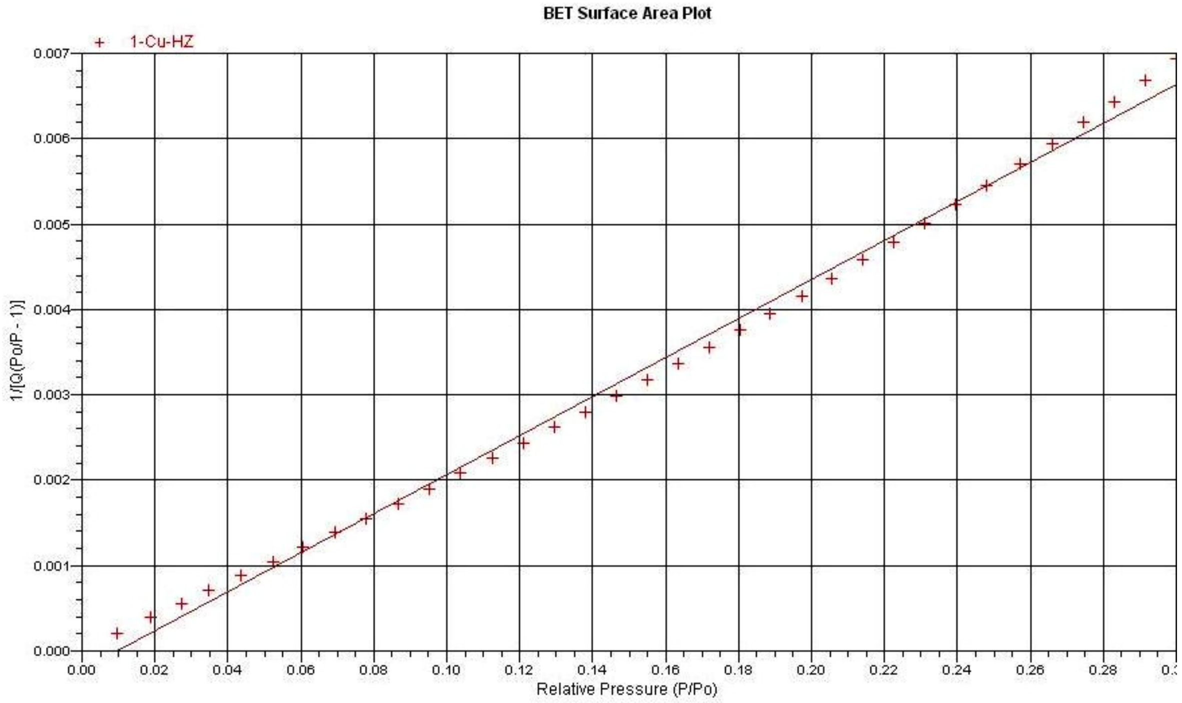


Figure F-7: BET surface area plot for CuO-ZnO-Al_2O_3 : HZSM-5=1

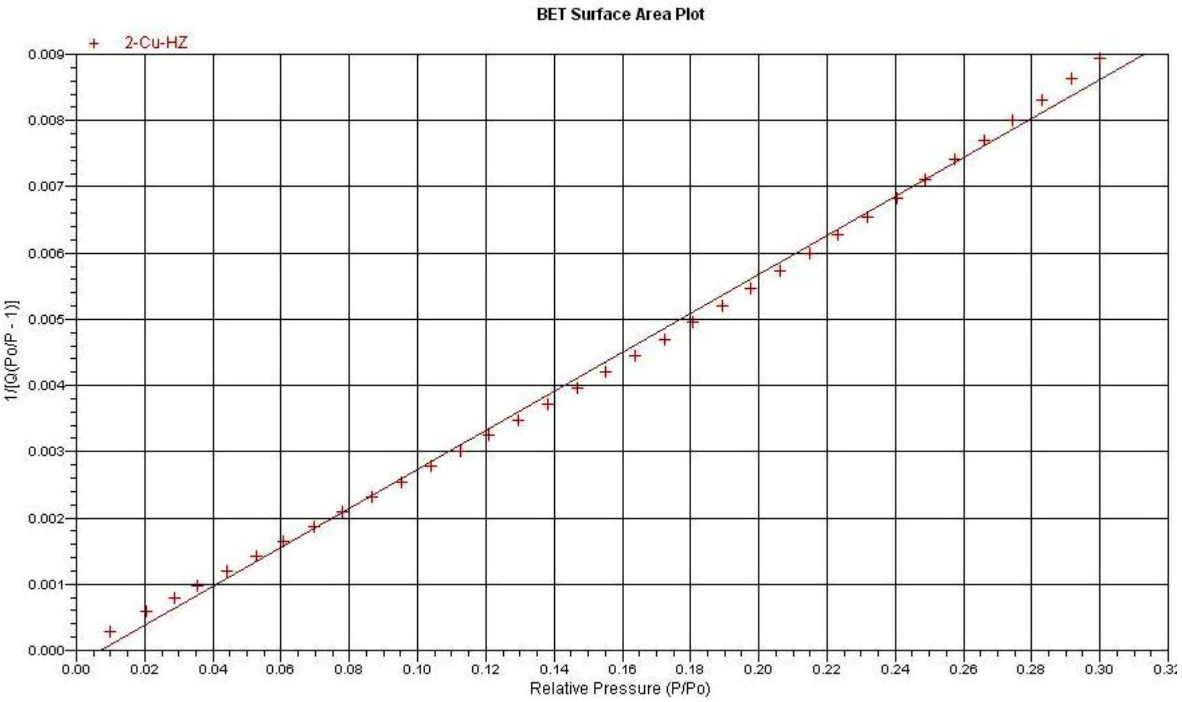


Figure F-8: BET surface area plot for CuO-ZnO-Al_2O_3 : HZSM-5=2

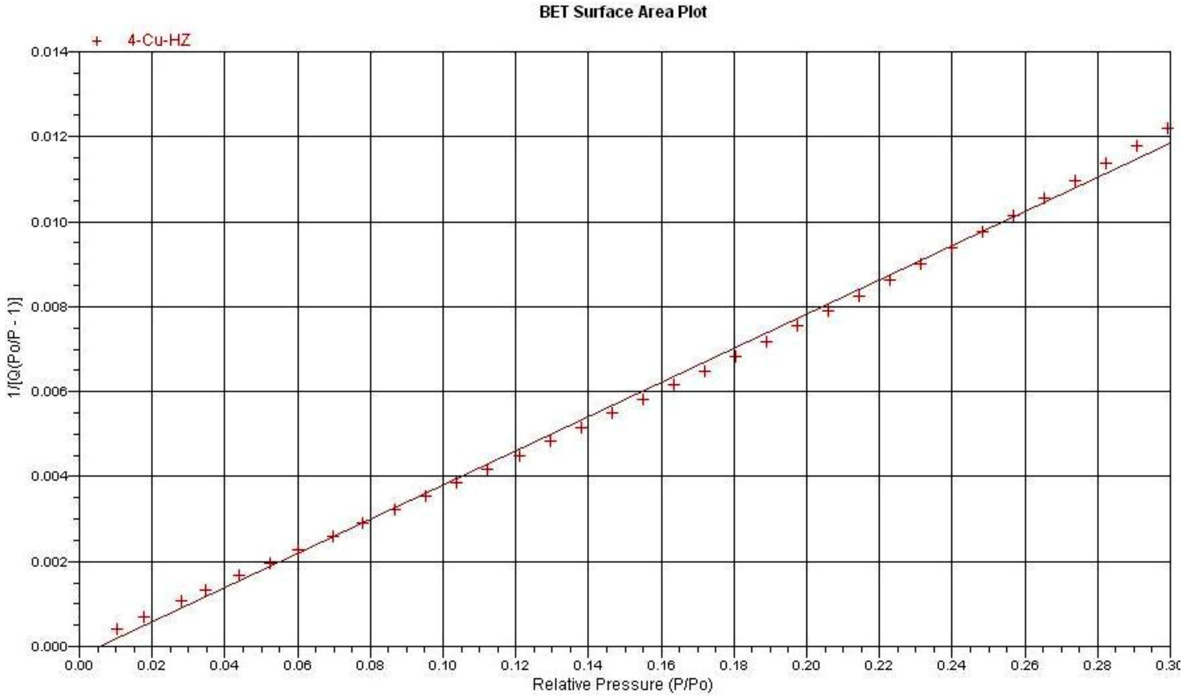


Figure F-9: BET surface area plot for CuO-ZnO-Al_2O_3 : HZSM-5=4

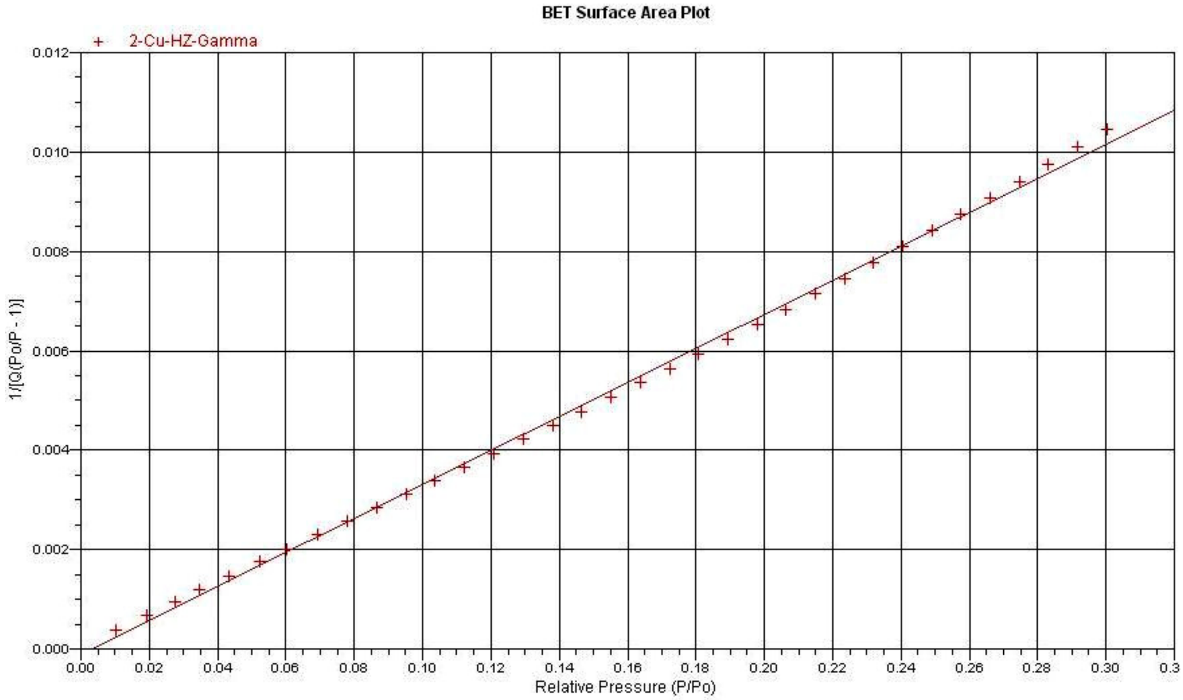


Figure F-10: BET surface area plot for CuO-ZnO-Al_2O_3 : (50%HZSM-5+50%γ- Al_2O_3)=2

F.3 BET isotherm plots

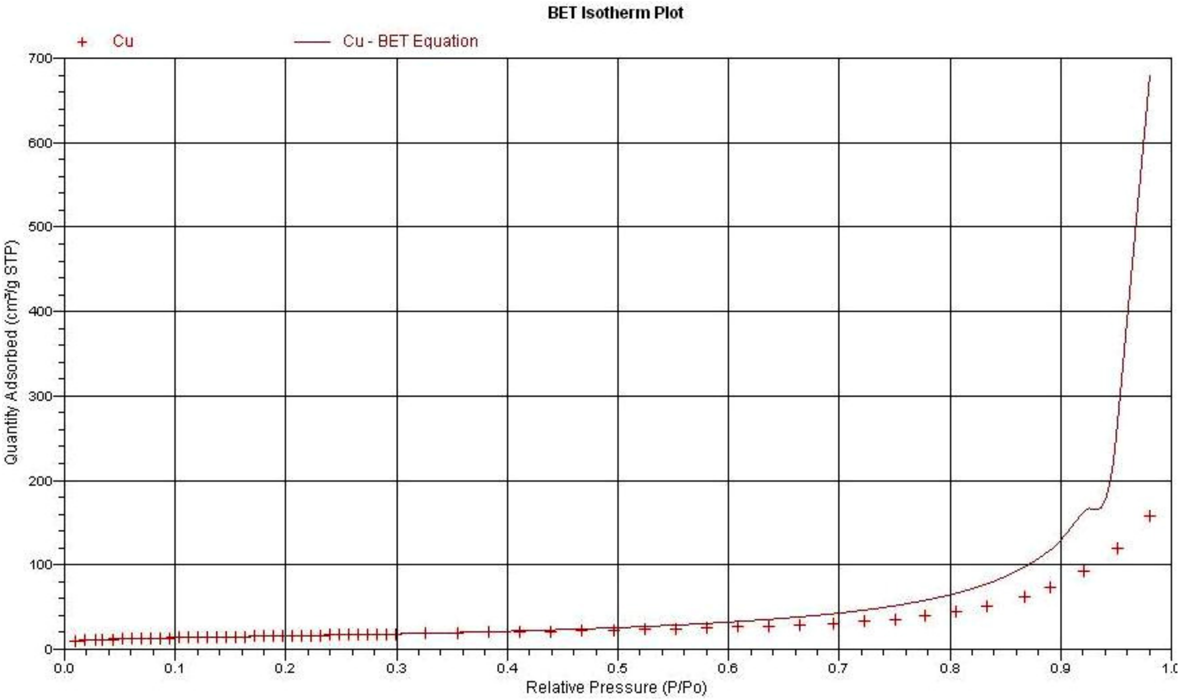


Figure F-11: BET isotherm plot for CuO-ZnO-Al_2O_3

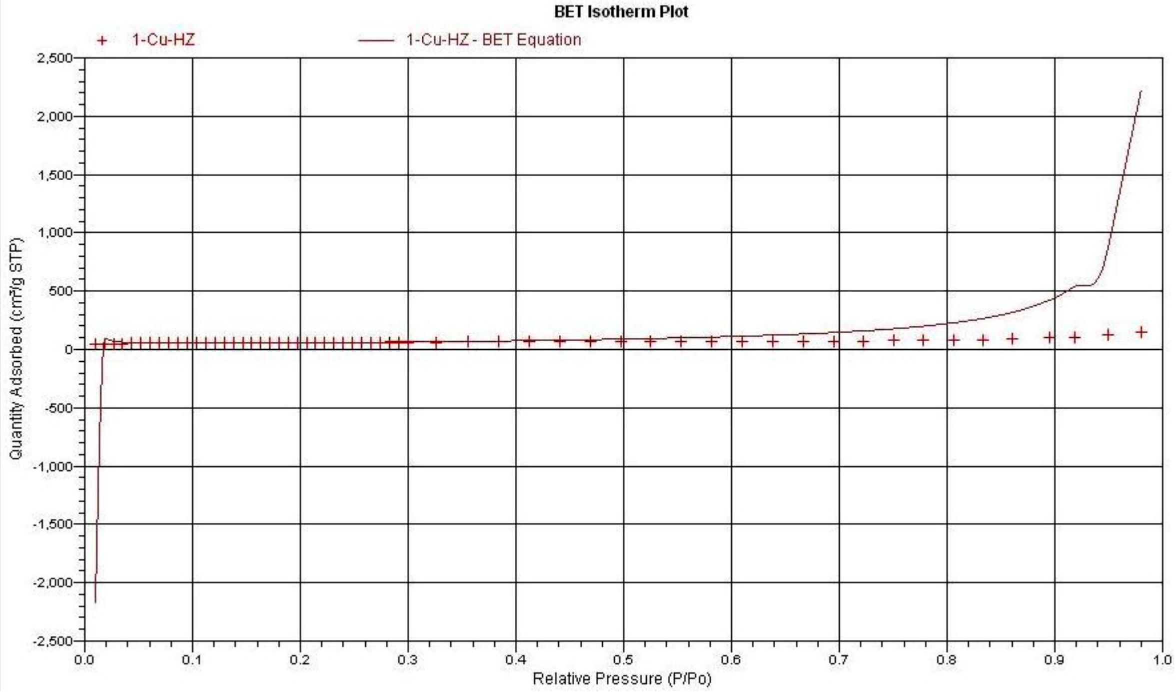


Figure F-12: BET isotherm plot for CuO-ZnO-Al_2O_3 : HZSM-5=1

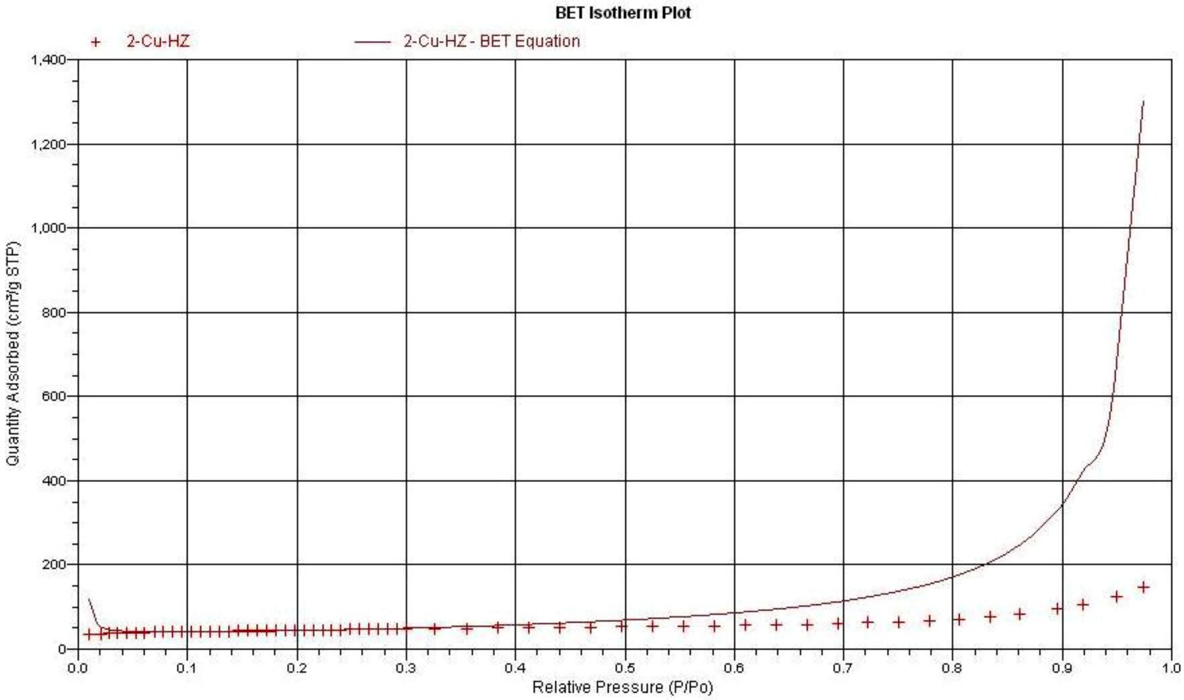


Figure F-13: BET isotherm plot for CuO-ZnO-Al_2O_3 : HZSM-5=2

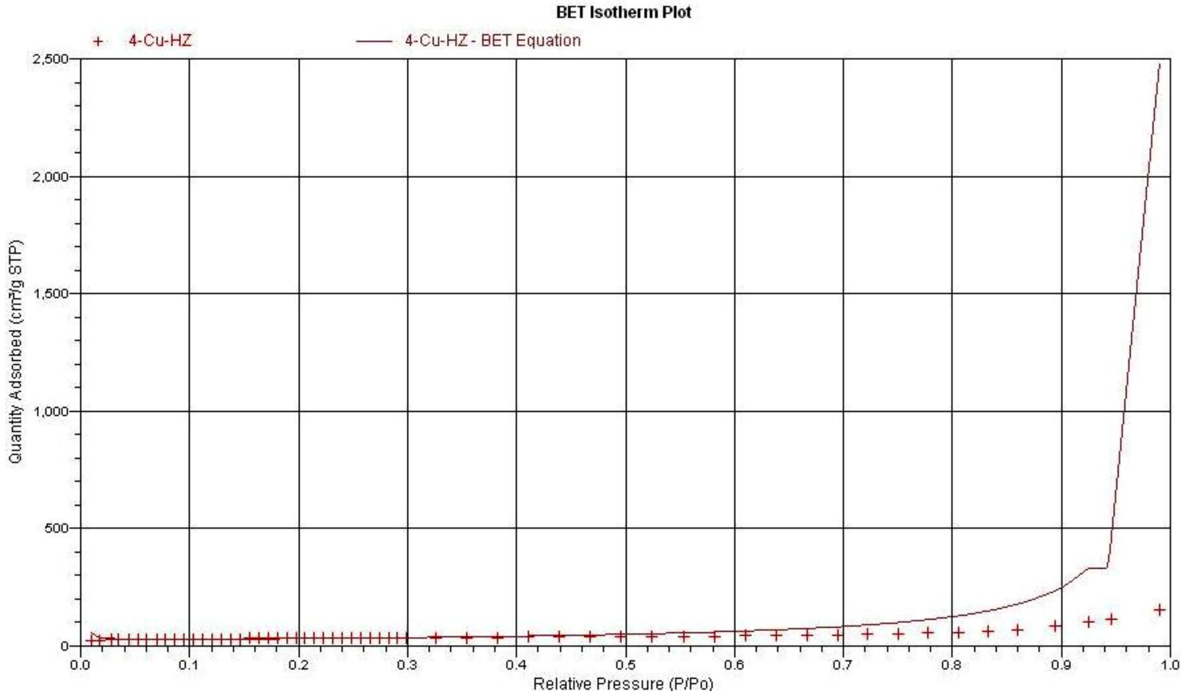


Figure F-14: BET isotherm plot for CuO-ZnO-Al_2O_3 : HZSM-5=4

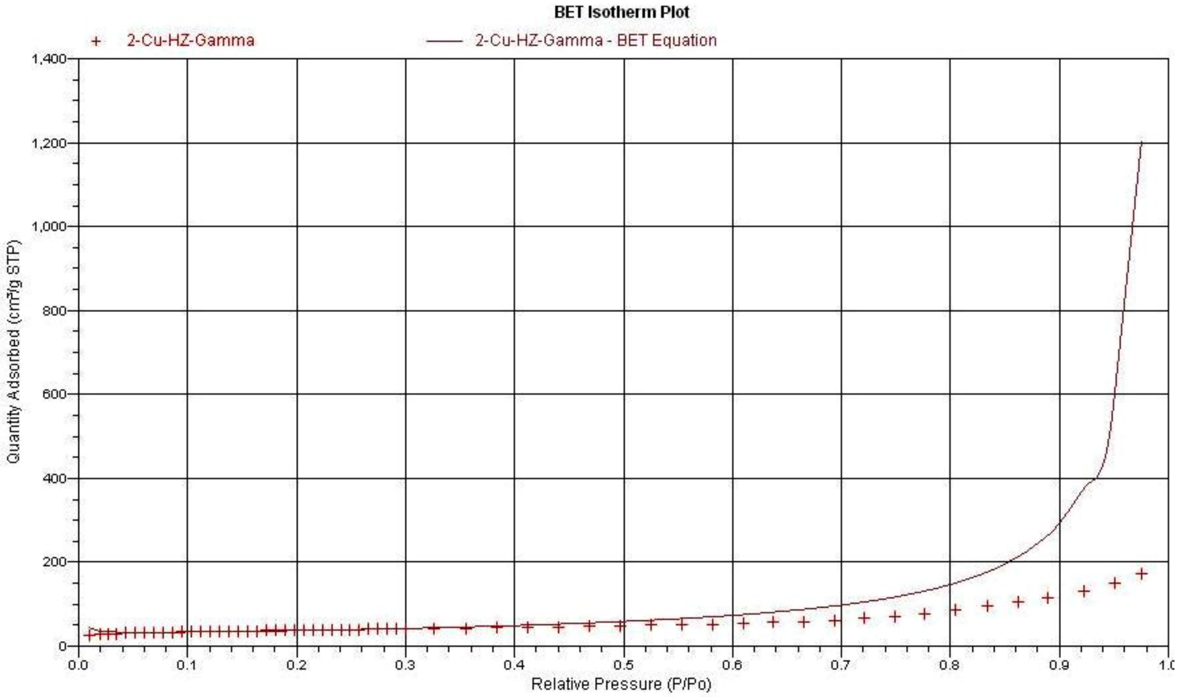


Figure F-15: BET isotherm plot for CuO-ZnO-Al_2O_3 : (50%HZSM-5+50%γ- Al_2O_3)=2

G GC DATA

G.1 Mole fractions of the product gases

RATIO = 1			Mol (%)							
FEED	Q	T	H2	N2	CO	CH4	CO2	CH4	DME	MeOH
2	150	255	61.25	5.51	23.69	6.37	5.4	6	1.82	0.24797
2	500	255	62.12	5.15	25.984	5.96	4.779	5.603	0.5286	0.12482
2	1000	255	62.156	5.044	26.428	5.868	4.901	5.46	0.24215	0.074223
2	250	255	61.33	5.206	25.034	6.032	5.581	5.713	0.9462	0.17277
2	75	255	58.87	5.74	20.75	6.61	8.1	6.32	3.08	0.339
2	150	255	60.55	5.364	23.887	6.19	6.276	5.863	1.5149	0.236
2	75	275	55.63	6.336	15.24	7.453	11.842	7.815	5.176	0.56156
2	75	235	60.706	5.272	24.413	6.113	5.904	5.747	1.289	0.18767

RATIO = 2			Mol (%)							
FEED	Q	T	H2	N2	CO	CH4	CO2	CH4	DME	MeOH
2	150	255	60.264	5.737	21.648	6.634	5.919	6.144	2.8747	0.455778
2	500	255	61.36	5.217	25.299	6.027	5.131	5.5422	0.8049	0.2748
2	75	255	56.511	6.172	17.26	7.14	10.087	6.563	4.995	0.615789
2	1000	255	61.676	5.086	26.0928	5.905	5.0586	5.4468	0.36853	0.19967
2	250	255	60.196	5.334	23.846	6.202	6.302	5.7276	1.5433	0.3918
1	75	255	37.494	6.6477	33.385	6.70156	10.06932	6.2549	5.5019	0.52626
3	75	255	75.7656	5.7428	7.603	6.28298	6.53487	5.8602	3.99176	0.713015
2	150	255	60.248	5.597	21.61429	6.38773	5.97435	5.91163	2.6419	0.580264
2	75	275	53.92477	6.849	11.539	7.96874	12.12524	7.61554	8.0164	1.00062
2	75	235	60.19485	5.45347	22.44983	6.3425	6.15864	6.07869	2.31856	0.591424

RATIO = 4			Mol (%)							
FEED	Q	T	H2	N2	CO	CH4	CO2	CH4	DME	MeOH
2	150	255	58.77	6.03	18.31	6.92	7.66	6.42	4.36	0.65
2	500	255	60.96	5.26	24.13	5.98	5.55	5.68	1.27	0.47
2	75	255	54.85	6.48	13.83	7.49	11.79	6.9	6.56	0.848
2	1000	255	61.6	5.07	25.54	5.75	5.1	5.51	0.514	0.323
2	250	255	59.4	5.46	22.12	6.33	7.078	5.87	2.25	0.588
2	150	255	58.215	5.748	19.516	6.639	8.492	6.1386	3.5592	0.686444
1	75	255	31.64	6.96	31.21	7.85	12.85	7.4	7.61	0.762
3	75	255	76.14	5.68	5.59	5.76	7.49	5.48	4.78	0.831
2	75	275	57.14	7.15	6.9	7.22	12.32	6.9	9.87	1.19
2	75	235	59.77	5.65	20.98	6.6	6.24	6.31	3.08	0.651

APPENDIX B: GC DATA

RATIO = 6			Mol (%)							
FEED	**Q**	**T**	**H2**	**N2**	**CO**	**CH4**	**CO2**	**CH4**	**DME**	**MeOH**
2	**75**	**255**	54.585	7.468	13.383	8.451	10.664	8.07	8.189	0.5267
2	**75**	**275**	49.325	8.007	8.798	9.539	14.766	9.745	10.363	0.8714
2	**75**	**235**	57.171	5.983	23.421	7.07	7.4677	6.669	2.95959	0.293698
2	**75**	**255**	51.392	7.1	14.503	8.4365	13.34	7.9284	7.35	0.530794
1	**75**	**255**	32.547	7.369	27.301	7.948	15.785	8.199	7.9959	0.56697
3	**75**	**255**	76.736	6.265	4.86	7.383	7.327	7.113	5.5023	0.639434
2	**75**	**255**	55.21	7.155	12.164	7.527	11.951	7.268	7.978	0.705966
2	**150**	**255**	55.415	6.532	18.917	7.713	9.345	7.531	5.242	0.57084
2	**250**	**255**	56.646	5.923	22.282	7.008	8.389	6.91	3.261	0.41945
2	**500**	**255**	58.258	5.552	25.0739	6.43	6.66989	6.3455	1.678	0.286062
2	**1000**	**255**	59.443	5.324	26.782	6.281	5.538	6.046	0.748819	0.16918
2	**75**	**255**	51.666	6.954	14.184	8.21	13.4756	7.969	7.4568	0.482044

RATIO = 8			Mol (%)							
FEED	**Q**	**T**	**H2**	**N2**	**CO**	**CH4**	**CO2**	**CH4**	**DME**	**MeOH**
2	**75**	**255**	53.135	7.174	13.962	8.383	11.457	8.197	7.92	0.52917
2	**75**	**275**	50.255	7.6259	10.371	9.081	14.359	9.304	9.18	0.712259
2	**75**	**235**	57.2166	5.9157	22.5448	6.9777	7.67	6.681	3.1913	0.32628
2	**75**	**255**	51.742	6.912	14.127	8.14989	12.825	7.90478	7.44582	0.621776
1	**75**	**255**	31.24	7.355	28.352	8.245	14.556	8.73	8.342	0.552859
3	**75**	**255**	78.222	6.0744	4.679	6.634	6.75	6.655	5.374	0.645791
3	**250**	**255**	76.896	5.301	11.344	6.335	5.5228	6.153	2.169	0.421636
3	**1000**	**255**	77.125	4.883	14.516	5.803	4.8387	5.643	0.571588	0.17539
1	**1000**	**255**	42.763	5.39	40.534	6.198	5.23077	6.0899	0.863793	0.130157
1	**250**	**255**	38.071	5.968	36.694	6.898	9.36684	7.0769	3.19253	0.309288
2	**75**	**255**	53.55	7.194	13.09157	8.05888	11.92934	7.74	8.07219	0.645453
2	**150**	**255**	55.781	6.3447	19.584	7.5105	8.83886	7.261	4.82668	0.511152
2	**250**	**255**	57.196	5.817	22.901	6.88097	7.66659	6.6552	2.87881	0.377431
2	**500**	**255**	58.8727	5.48784	25.56655	6.34416	6.22087	6.1806	1.43384	0.231038
2	**1000**	**255**	59.8	5.3063	26.921	6.12259	5.49181	5.964	0.67707	0.137886
2	**75**	**255**	5165676	6.91277	14.40415	8.15655	13.19694	7.78928	7.34869	0.652511

G.2 Mass balances

FEED ANALYSIS		mMol/min										
FEED	**Q**	H2	N2	CO	CH4	CO2						
1	**75**	1.43538	0.17245	1.39502	0.20071	0.14466						
2	**75**	2.01293	0.15774	0.84681	0.17993	0.15081						
3	**75**	2.38886	0.14922	0.48843	0.17944	0.14226						
Ratio 1-1		mMol/min					mMol/min					**Carbon Balance**
FEED	**Q**	H2	N2	CO	CH4	CO2	CH4	DME	MeOH	Carbon OUT	Carbon IN	**Error %**
2	**150**	3.50692	0.31548	1.35639	0.36472	0.30918	0.36472	0.11063	0.01507	31.57618332	28.261142	11.73003179
2	**500**	12.6845	1.0516	5.30578	1.217	0.97584	1.217	0.11481	0.02711	107.6682232	94.203808	14.29285684
2	**1000**	25.9172	2.1032	11.0197	2.44678	2.04357	2.44678	0.10851	0.03326	218.4853809	188.40762	15.96419827
2	**250**	6.19425	0.5258	2.5284	0.60922	0.56367	0.60922	0.1009	0.01842	54.36902463	47.101904	15.42850741
2	**75**	1.6178	0.15774	0.57023	0.18165	0.22259	0.18165	0.08852	0.00974	16.11492802	14.130571	14.04300526
2	**150**	3.5612	0.31548	1.4049	0.36406	0.36912	0.36406	0.09407	0.01465	32.45908301	28.261142	14.85410825
2	**75**	1.38495	0.15774	0.37941	0.18555	0.29482	0.18555	0.12289	0.01333	15.65329999	14.130571	10.7761307
2	**75**	1.81634	0.15774	0.73044	0.1829	0.17665	0.1829	0.04102	0.00597	16.3310309	14.130571	15.57233398
Ratio 2-1		H2	N2	CO	CH4	CO2	CH4	DME	MeOH	Carbon OUT	Carbon IN	**Error %**
2	**150**	3.31394	0.31548	1.19043	0.36481	0.32549	0.36481	0.17069	0.02706	31.36764049	28.261142	10.99211814
2	**500**	12.3684	1.0516	5.09956	1.21487	1.03426	1.21487	0.17644	0.06024	107.7201553	94.203808	14.34798425
2	**75**	1.44427	0.15774	0.44112	0.18248	0.2578	0.18248	0.13888	0.01712	16.30513423	14.130571	15.389067
2	**1000**	25.5047	2.1032	10.7901	2.44188	2.09187	2.44188	0.16522	0.08951	218.2277517	188.40762	15.82745796
2	**250**	5.93383	0.5258	2.35062	0.61136	0.62122	0.61136	0.16473	0.04182	54.7902091	47.101904	16.32270582
1	**75**	0.97264	0.17245	0.86605	0.17385	0.26121	0.17385	0.15292	0.01463	21.5450527	20.884586	3.162460784
3	**75**	1.9687	0.14922	0.19756	0.16326	0.1698	0.16326	0.11121	0.01986	11.23379552	9.7215593	15.55548999
2	**150**	3.39593	0.31548	1.21831	0.36005	0.33675	0.36005	0.16091	0.03534	31.58772032	28.261142	11.77085464
2	**75**	1.24195	0.15774	0.26576	0.18353	0.27926	0.18353	0.19319	0.02411	15.87075218	14.130571	12.31500832
2	**75**	1.74112	0.15774	0.64935	0.18345	0.17814	0.18345	0.06997	0.01785	16.22637161	14.130571	14.83167533

APPENDIX G: GC DATA

Ratio 4-1		mMol/min					mMol/min					Carbon Balance
FEED	**Q**	H2	N2	CO	CH4	CO2	CH4	DME	MeOH	Carbon OUT	Carbon IN	**Error %**
2	**150**	3.07475	0.31548	0.95795	0.36204	0.40076	0.36204	0.24587	0.03666	31.33435582	28.261142	10.87434276
2	**500**	12.1874	1.0516	4.82416	1.19554	1.10958	1.19554	0.26731	0.09893	107.5005608	94.203808	14.11487853
2	**75**	1.33519	0.15774	0.33666	0.18233	0.287	0.18233	0.17334	0.02241	16.28879159	14.130571	15.27341249
2	**1000**	25.5536	2.1032	10.5948	2.38528	2.11564	2.38528	0.22251	0.13983	216.7904187	188.40762	15.06457321
2	**250**	5.72024	0.5258	2.13016	0.60958	0.68161	0.60958	0.23366	0.06106	54.71171533	47.101904	16.15605911
2	**150**	3.19514	0.31548	1.07114	0.36438	0.46608	0.36438	0.21127	0.04075	32.75131958	28.261142	15.88816614
1	**75**	0.78395	0.17245	0.7733	0.1945	0.31839	0.1945	0.20002	0.02003	22.80916806	20.884586	9.215323746
3	**75**	2.0003	0.14922	0.14686	0.15132	0.19677	0.15132	0.13199	0.02295	11.19852959	9.7215593	15.19272994
2	**75**	1.2606	0.15774	0.15222	0.15928	0.2718	0.15928	0.22785	0.02747	14.70903199	14.130571	4.093683198
2	**75**	1.66869	0.15774	0.58573	0.18426	0.17421	0.18426	0.08994	0.01901	15.92832788	14.130571	12.7224632
Ratio 6-1		H2	N2	CO	CH4	CO2	CH4	DME	MeOH	Carbon OUT	Carbon IN	**Error %**
2	**75**	1.18997	0.1628	0.29175	0.18423	0.23248	0.18423	0.18695	0.01202	15.34350158	14.130571	8.583732361
2	**75**	1.00291	0.1628	0.17889	0.19395	0.30023	0.19395	0.20625	0.01734	15.56257753	14.130571	10.13410104
2	**75**	1.55569	0.1628	0.63731	0.19238	0.2032	0.19238	0.08538	0.00847	16.85410253	14.130571	19.27403589
2	**75**	1.17843	0.1628	0.33256	0.19345	0.30589	0.19345	0.17934	0.01295	16.76368422	14.130571	18.63415864
1	**75**	0.76167	0.17245	0.6389	0.186	0.3694	0.186	0.18139	0.01286	21.07140087	20.884586	0.894511425
3	**75**	1.82772	0.14922	0.11576	0.17585	0.17452	0.17585	0.13603	0.01581	11.15811206	9.7215593	14.77697841
2	**75**	1.25624	0.1628	0.27678	0.17127	0.27193	0.17127	0.188	0.01664	15.40661561	14.130571	9.0303812
2	**150**	2.76234	0.32561	0.94298	0.38448	0.46583	0.38448	0.26762	0.02914	32.90583292	28.261142	16.43490038
2	**250**	5.19006	0.54268	2.04154	0.64209	0.76862	0.64209	0.30302	0.03898	56.87230838	47.101904	20.74312008
2	**500**	11.3889	1.08536	4.90171	1.257	1.3039	1.257	0.3324	0.05667	113.2929924	94.203808	20.26370811
2	**1000**	24.2364	2.17073	10.9197	2.56092	2.25798	2.56092	0.31718	0.07166	228.0661369	188.40762	21.04931972
2	**75**	1.20958	0.1628	0.33207	0.19221	0.31549	0.19221	0.17986	0.01163	16.83974759	14.130571	19.17244808
Ratio 8-1		H2	N2	CO	CH4	CO2	CH4	DME	MeOH	Carbon OUT	Carbon IN	**Error %**
2	**75**	1.20583	0.1628	0.31685	0.19024	0.26	0.19024	0.18381	0.01228	16.04686187	14.130571	13.56131103
2	**75**	1.07289	0.1628	0.22141	0.19387	0.30655	0.19387	0.19129	0.01484	15.7572996	14.130571	11.5121209
2	**75**	1.57464	0.1628	0.62045	0.19203	0.21108	0.19203	0.09173	0.00938	16.90115019	14.130571	19.60698535
2	**75**	1.21872	0.1628	0.33275	0.19196	0.30208	0.19196	0.18082	0.0151	16.74574367	14.130571	18.50719604
1	**75**	0.73247	0.17245	0.66476	0.19332	0.34129	0.19332	0.18473	0.01224	21.29253859	20.884586	1.953367557
3	**75**	1.92157	0.14922	0.11494	0.16297	0.16582	0.16297	0.1316	0.01581	10.62852448	9.7215593	9.329420523
3	**250**	7.21533	0.49741	1.06443	0.59443	0.51822	0.59443	0.20954	0.04073	38.77589817	32.405198	19.65950166
3	**1000**	31.4253	1.98962	5.91467	2.36448	1.97157	2.36448	0.2395	0.07349	158.0124101	129.62079	21.90359951
1	**1000**	18.2424	2.29933	17.2915	2.64402	2.23141	2.64402	0.37503	0.05651	307.4103594	278.46114	10.39614148
1	**250**	3.66697	0.57483	3.53434	0.66441	0.90221	0.66441	0.29973	0.02904	76.72638536	69.615286	10.21485299
2	**75**	1.21187	0.1628	0.29627	0.18238	0.26997	0.18238	0.1902	0.01521	15.919319	14.130571	12.65870865
2	**150**	2.86267	0.32561	1.00505	0.38544	0.45361	0.38544	0.25622	0.02713	33.22915418	28.261142	17.57894916
2	**250**	5.33595	0.54268	2.13649	0.64194	0.71523	0.64194	0.27768	0.03641	56.72848683	47.101904	20.43777881
2	**500**	11.6436	1.08536	5.05645	1.25472	1.23034	1.25472	0.29108	0.0469	113.1036215	94.203808	20.06268556
2	**1000**	24.4633	2.17073	11.013	2.50466	2.24661	2.50466	0.28434	0.05791	226.7458862	188.40762	20.34857801
2	**75**	121658	0.1628	0.33924	0.1921	0.3108	0.1921	0.18123	0.01609	16.9534674	14.130571	19.97722665

H HSE COURSES

Hei,

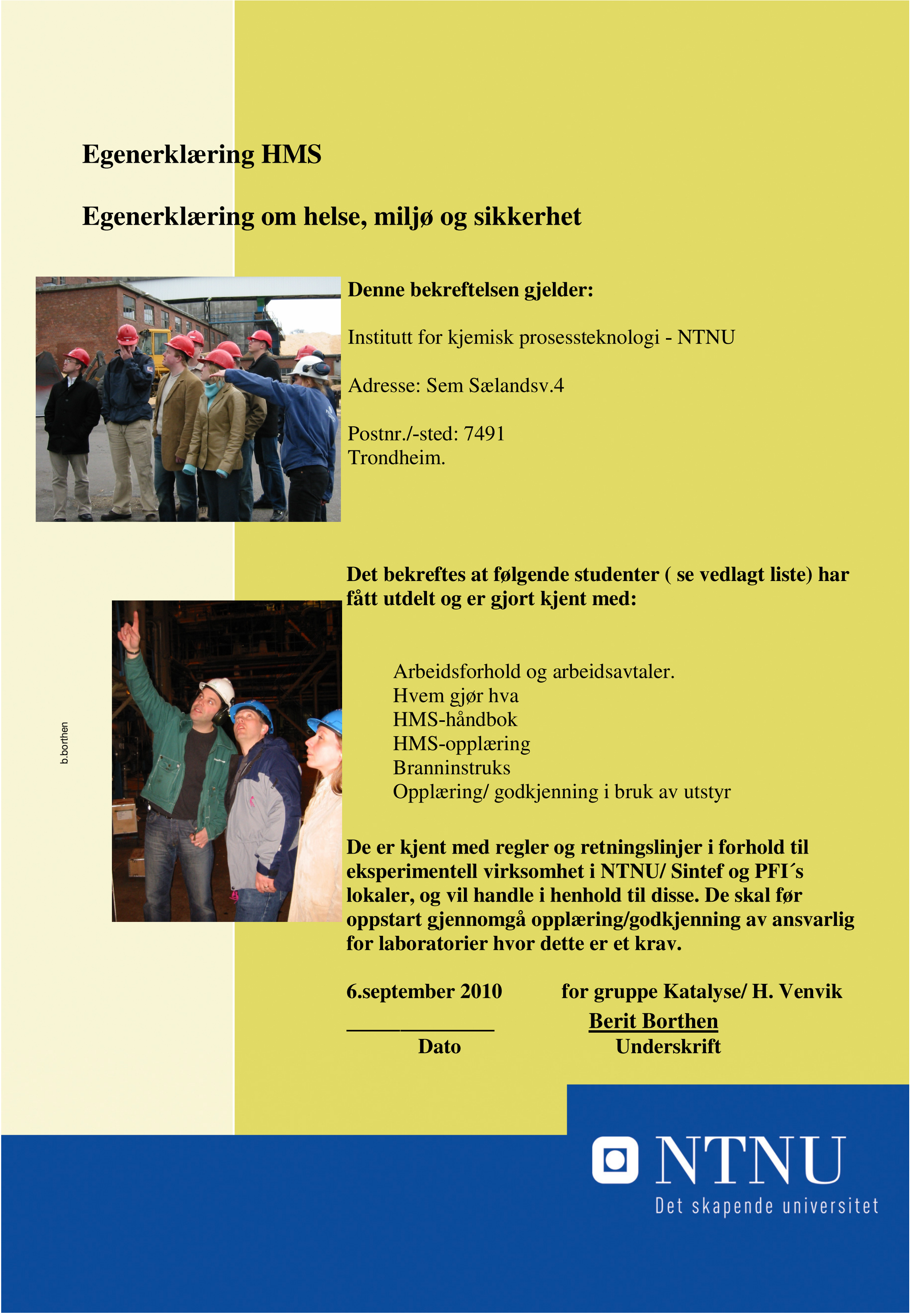
Det bekreftes herved at følgende studenter har gjennomgått IKPs HMS-introduksjonskurs. Dette omfatter sikkerhetskurset og opplæring i bruk av gass og flaskeregulatorer. Varighet ca 2 timer.

mvh

Berit

HSE-Security course 6. sept.

Master:	1-Sep	2-Sep	6-Sep
Aina Elin Karlsen	x	x	x
Juan Bautista Freire Lopez	x	x	x
Claire Barilleau	x	x	x
Katrine Plûnnecke	x	x	
Huu Nguyen Loc	x	x	x
Dimitri Viatkin			
Mario Jimenez Ortega	x	x	x
Ida Lien Bjørnstad	x	x	
Vegar Evenrud	x	x	x
Damien Vannies	x	x	x
Kimete Osmani	x	x	
Mahmud Alam	x	x	x
Ayob Esmael Pour	x	x	x
Phd and post doc:			
Nicla Vicinanza	x	x	
Charita Udani	x	x	
Georg Voss	x	x	x
Javi Fermoso Domigues	x	x	x
Andrey Volynkin	x	x	x
Fengiliu Lou	x		
Sulalit Bandyopadhyay	x	x	x
Karen N. Seglem			x



Egenerklæring HMS

Egenerklæring om helse, miljø og sikkerhet

Denne bekreftelsen gjelder:

Institutt for kjemisk prosessteknologi - NTNU

Adresse: Sem Sælandsv.4

Postnr./-sted: 7491
Trondheim.

Det bekreftes at følgende studenter (se vedlagt liste) har fått utdelt og er gjort kjent med:

Arbeidsforhold og arbeidsavtaler.
Hvem gjør hva
HMS-håndbok
HMS-opplæring
Branninstruks
Opplæring/ godkjenning i bruk av utstyr

b.borthen

De er kjent med regler og retningslinjer i forhold til eksperimentell virksomhet i NTNU/ Sintef og PFI´s lokaler, og vil handle i henhold til disse. De skal før oppstart gjennomgå opplæring/godkjenning av ansvarlig for laboratorier hvor dette er et krav.

6.september 2010 **for gruppe Katalyse/ H. Venvik**

______________ **Berit Borthen**

Dato **Underskrift**

NTNU
Det skapende universitet

1036313130

TRAINOR

Certificate

of core competence awarded June 15th 2010 to

Ayob Ismael Por

On successfully completing and passing the interactive course

NTNU-SINTEF - Health, Safety & Environment in the laboratories

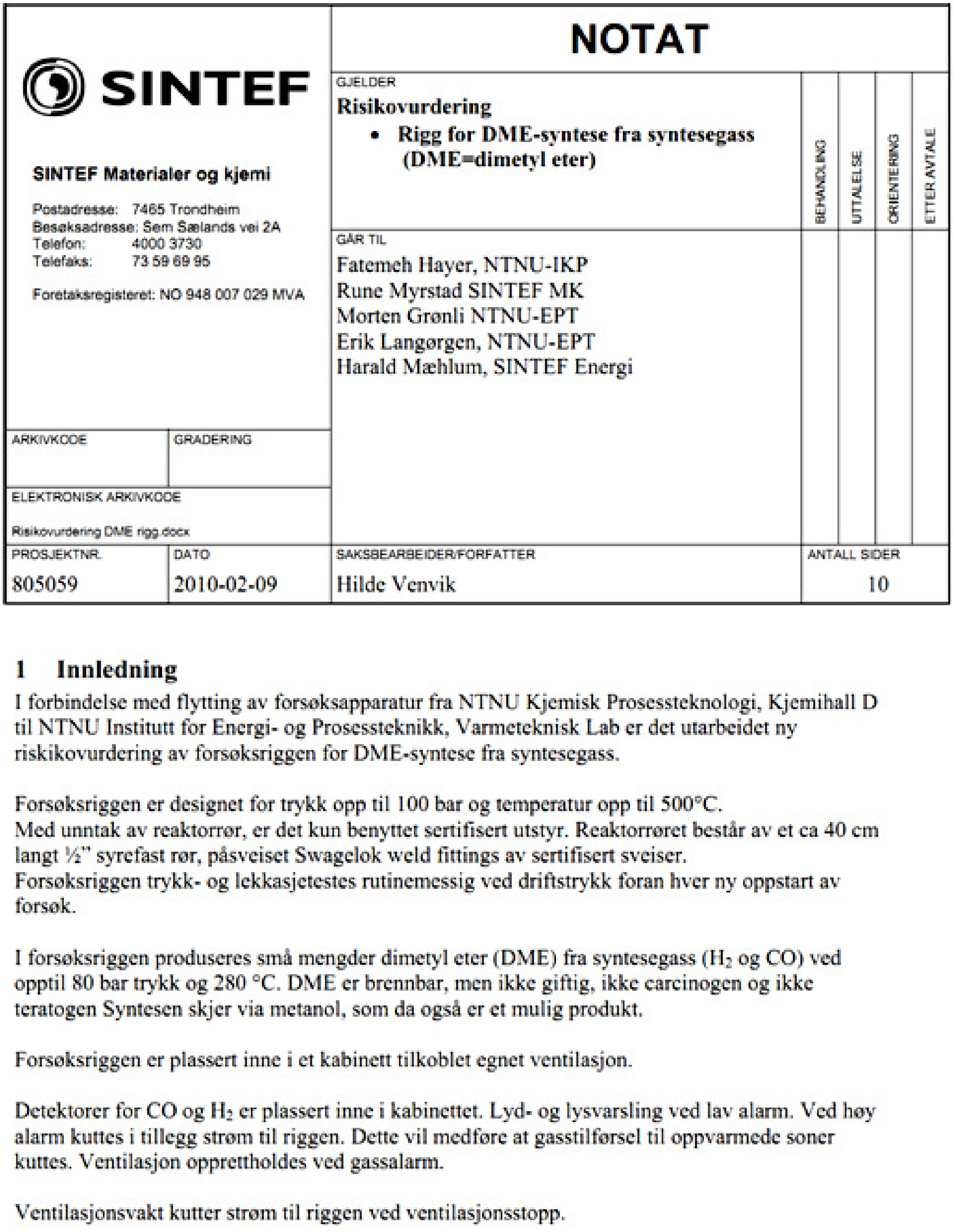
The training was performed in accordance to ISO 9001
with relevant procedures, regulations and standards from IEC/CENELEC/NEK/DSB/NEMKO
Course specifics found on seperate appendix - ref 1036313130, www.trainor.no

Ranveig M. Eldevik
Ranveig Morberg Eldevik
Course manager

Terje Gravdal
Terje Gravdal
Managing Director

Trainor AS • Prestegaten 3-5 • Postboks 554 Sentrum • NO-3101 Tønsberg • t +47 33 37 89 00 • f +47 33 37 89 01 • post@trainor.no • www.trainor.no

I RISK ASSESSMENT



SINTEF

SINTEF Materialer og kjemi

Postadresse: 7465 Trondheim
Besøksadresse: Sem Sælands vei 2A
Telefon: 4000 3730
Telefaks: 73 59 69 95

Foretaksregisteret: NO 948 007 029 MVA

NOTAT

GJELDER

Risikovurdering

- **Rigg for DME-syntese fra syntesegass (DME=dimetyl eter)**

BEHANDLING	UTTALELSE	ORIENTERING	ETTER AVTALE

GÅR TIL

Fatemeh Hayer, NTNU-IKP
Rune Myrstad SINTEF MK
Morten Grønli NTNU-EPT
Erik Langørgen, NTNU-EPT
Harald Mæhlum, SINTEF Energi

ARKIVKODE	GRADERING

ELEKTRONISK ARKIVKODE

Risikovurdering DME rigg.docx

PROSJEKTNR.	DATO	SAKSBEARBEIDER/FORFATTER	ANTALL SIDER
805059	2010-02-09	Hilde Venvik	10

1 Innledning

I forbindelse med flytting av forsøksapparatur fra NTNU Kjemisk Prosessteknologi, Kjemihall D til NTNU Institutt for Energi- og Prosessteknikk, Varmeteknisk Lab er det utarbeidet ny riskikovurdering av forsøksriggen for DME-syntese fra syntesegass.

Forsøksriggen er designet for trykk opp til 100 bar og temperatur opp til 500°C.
Med unntak av reaktorrør, er det kun benyttet sertifisert utstyr. Reaktorrøret består av et ca 40 cm langt ½" syrefast rør, påsveiset Swagelok weld fittings av sertifisert sveiser.
Forsøksriggen trykk- og lekkasjetestes rutinemessig ved driftstrykk foran hver ny oppstart av forsøk.

I forsøksriggen produseres små mengder dimetyl eter (DME) fra syntesegass (H_2 og CO) ved opptil 80 bar trykk og 280 °C. DME er brennbar, men ikke giftig, ikke carcinogen og ikke teratogen Syntesen skjer via metanol, som da også er et mulig produkt.

Forsøksriggen er plassert inne i et kabinett tilkoblet egnet ventilasjon.

Detektorer for CO og H_2 er plassert inne i kabinettet. Lyd- og lysvarsling ved lav alarm. Ved høy alarm kuttes i tillegg strøm til riggen. Dette vil medføre at gasstilførsel til oppvarmede soner kuttes. Ventilasjon opprettholdes ved gassalarm.

Ventilasjonsvakt kutter strøm til riggen ved ventilasjonsstopp.

INNHOLDSFORTEGNELSE

2 Tegninger, foto, beskrivelse, prosedyrer

Foto av riggen er vist i Figur 2.1 Skisse av forsøksriggen er vist i Figur 2.2 Se mer detaljert beskrivelse av apparaturen i vedlegg 1.

2.1 Prosedyrer

- Før oppstart skal det foreligge:
  - Godkjent risikovurdering (dette notatet)
  - Apparaturkort
  - Rapport fra siste test og kalibrering av gassalarm-anlegg
  - Bekreftet operativt ventilasjonsanlegg
  - Tilgang kjelevann

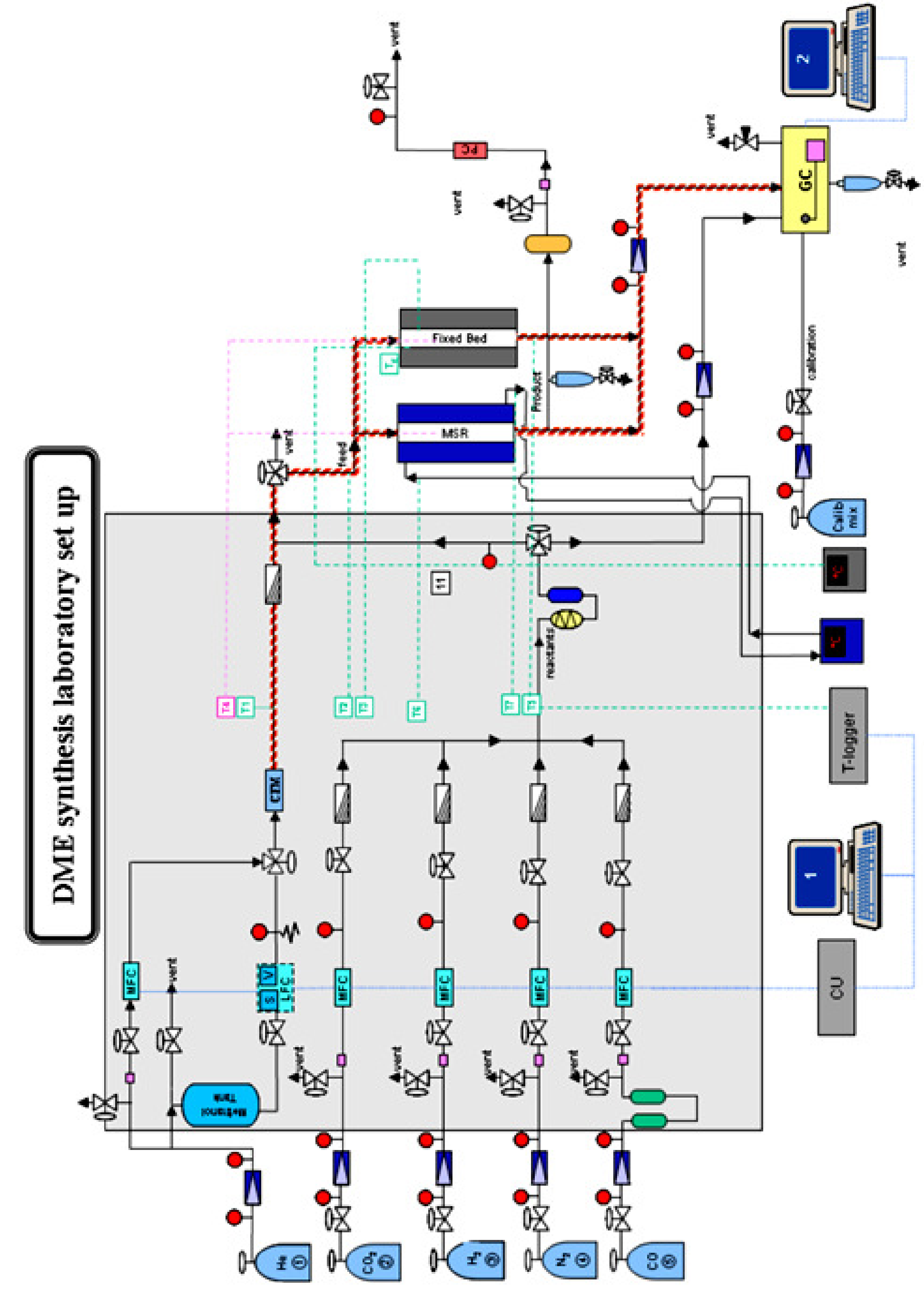
- Ved oppstart av forsøk

Labansvarlig varsles om planlagt oppstart og gir godkjenning
Det settes opp Forsøkskort som angir info om karakter, varighet og ansvarlige for forsøket
Utstyret lekkasjetestes opp til 1,2xforsøkstrykket, først under inert gass, dernest under hydrogen/syntesegass

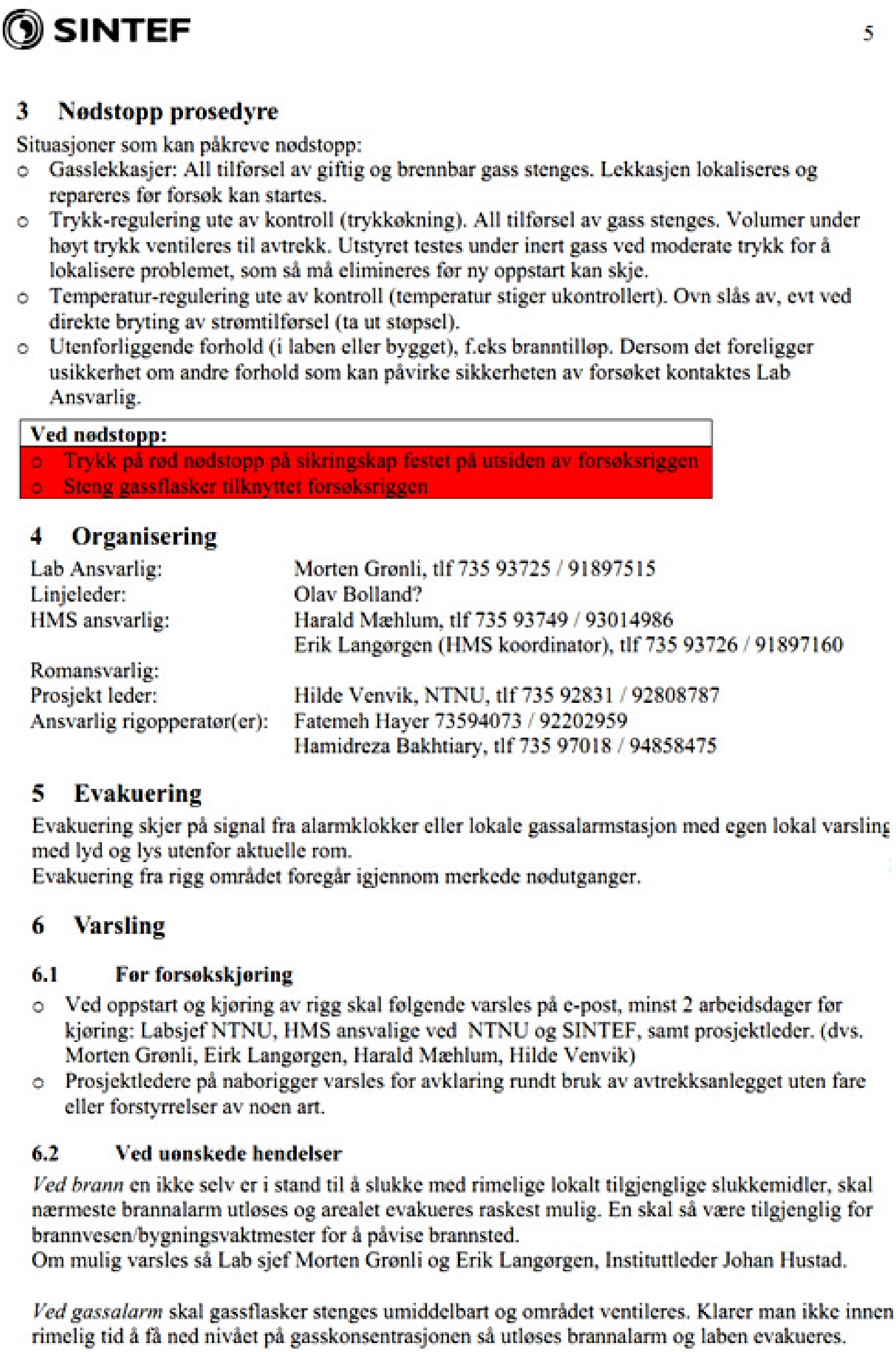
- Forsøk startes

Den ansvarlige rig-operatør skal se til forsøket jevnlig, men det gis anledning til å forlate forsøket under kjøring og overnatta i henhold til plan. Ved hvert tilsyn sjekkes for tegn på mindre lekkasjer, ennå ikke fanget opp av alarmanlegget, samt at trykk og temperatur reguleres som forutsatt. Ved gassalarm uten operatører til stede, se pkt 6 Varsling. I det følgende angis prosedyrer ved lekkasjer og avvik:

SINTEF



Skisse over forsøksrigg for metanolsyntese fra syntesegass



3 Nødstopp prosedyre

Situasjoner som kan påkreve nødstopp:

- Gasslekkasjer: All tilførsel av giftig og brennbar gass stenges. Lekkasjen lokaliseres og repareres før forsøk kan startes.
- Trykk-regulering ute av kontroll (trykkøkning). All tilførsel av gass stenges. Volumer under høyt trykk ventileres til avtrekk. Utstyret testes under inert gass ved moderate trykk for å lokalisere problemet, som så må elimineres før ny oppstart kan skje.
- Temperatur-regulering ute av kontroll (temperatur stiger ukontrollert). Ovn slås av, evt ved direkte bryting av strømtilførsel (ta ut støpsel).
- Utenforliggende forhold (i laben eller bygget), f.eks branntilløp. Dersom det foreligger usikkerhet om andre forhold som kan påvirke sikkerheten av forsøket kontaktes Lab Ansvarlig.

Ved nødstopp:

- Trykk på rød nødstopp på sikringskap festet på utsiden av forsøksriggen
- Steng gassflasker tilknyttet forsøksriggen

4 Organisering

Lab Ansvarlig:	Morten Grønli, tlf 735 93725 / 91897515
Linjeleder:	Olav Bolland?
HMS ansvarlig:	Harald Mæhlum, tlf 735 93749 / 93014986 Erik Langørgen (HMS koordinator), tlf 735 93726 / 91897160
Romansvarlig:	
Prosjekt leder:	Hilde Venvik, NTNU, tlf 735 92831 / 92808787
Ansvarlig rigopperatør(er):	Fatemeh Hayer 73594073 / 92202959 Hamidreza Bakhtiary, tlf 735 97018 / 94858475

5 Evakuering

Evakuering skjer på signal fra alarmklokker eller lokale gassalarmstasjon med egen lokal varsling med lyd og lys utenfor aktuelle rom.
Evakuering fra rigg området foregår igjennom merkede nødutganger.

6 Varsling

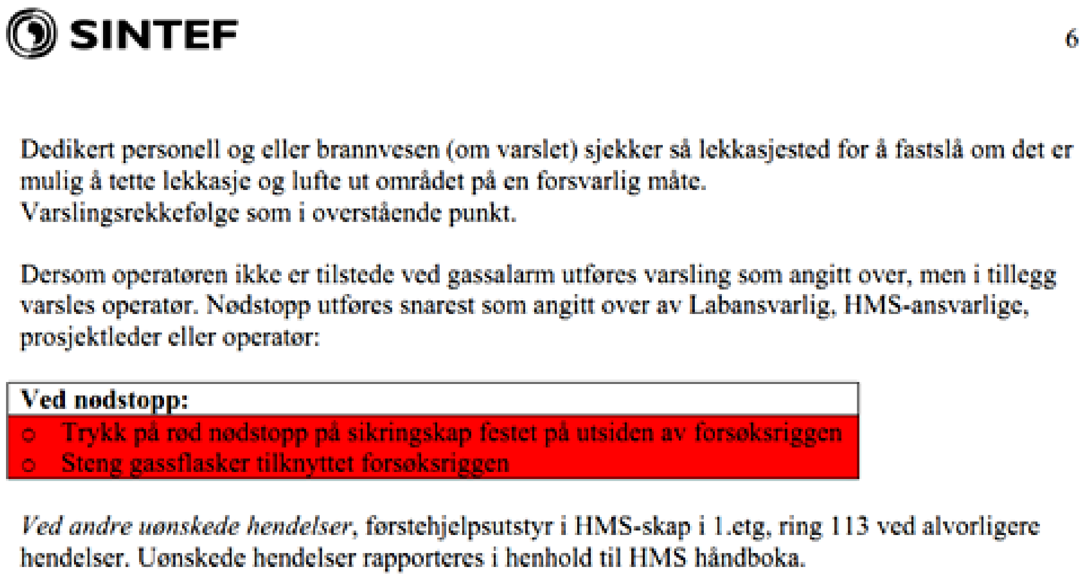
6.1 Før forsøkskjøring

- Ved oppstart og kjøring av rigg skal følgende varsles på e-post, minst 2 arbeidsdager før kjøring: Labsjef NTNU, HMS ansvalige ved NTNU og SINTEF, samt prosjektleder. (dvs. Morten Grønli, Eirk Langørgen, Harald Mæhlum, Hilde Venvik)
- Prosjektledere på naborigger varsles for avklaring rundt bruk av avtrekksanlegget uten fare eller forstyrrelser av noen art.

6.2 Ved uønskede hendelser

Ved brann en ikke selv er i stand til å slukke med rimelige lokalt tilgjenglige slukkemidler, skal nærmeste brannalarm utløses og arealet evakueres raskest mulig. En skal så være tilgjenglig for brannvesen/bygningsvaktmester for å påvise brannsted.
Om mulig varsles så Lab sjef Morten Grønli og Erik Langørgen, Instituttleder Johan Hustad.

Ved gassalarm skal gassflasker stenges umiddelbart og området ventileres. Klarer man ikke innen rimelig tid å få ned nivået på gasskonsentrasjonen så utløses brannalarm og laben evakueres.



SINTEF 6

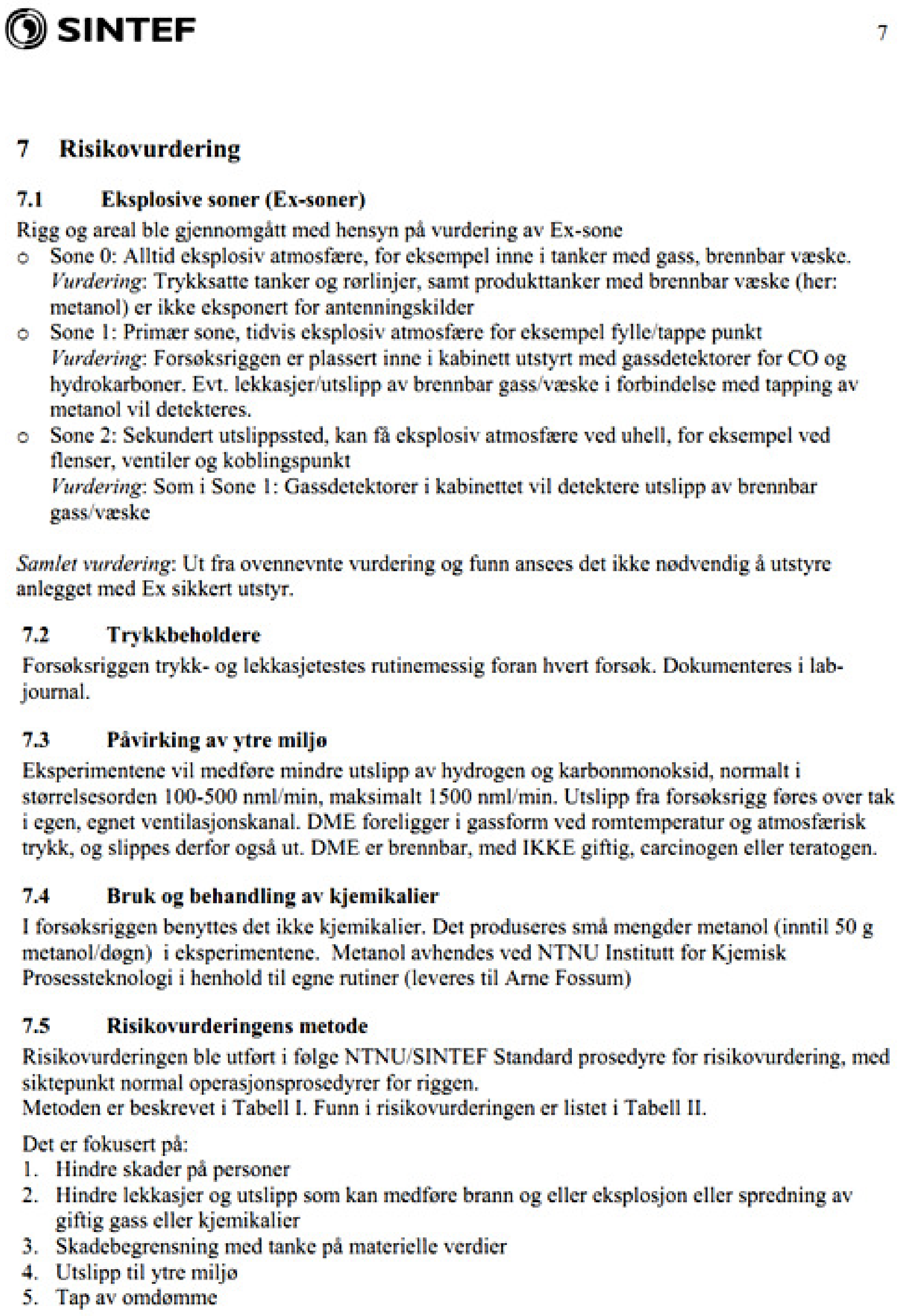
Dedikert personell og eller brannvesen (om varslet) sjekker så lekkasjested for å fastslå om det er mulig å tette lekkasje og lufte ut området på en forsvarlig måte.
Varslingsrekkefølge som i overstående punkt.

Dersom operatøren ikke er tilstede ved gassalarm utføres varsling som angitt over, men i tillegg varsles operatør. Nødstopp utføres snarest som angitt over av Labansvarlig, HMS-ansvarlige, prosjektleder eller operatør:

Ved nødstopp:

- Trykk på rød nødstopp på sikringskap festet på utsiden av forsøksriggen
- Steng gassflasker tilknyttet forsøksriggen

Ved andre uønskede hendelser, førstehjelpsutstyr i HMS-skap i 1.etg, ring 113 ved alvorligere hendelser. Uønskede hendelser rapporteres i henhold til HMS håndboka.



7 Risikovurdering

7.1 Eksplosive soner (Ex-soner)

Rigg og areal ble gjennomgått med hensyn på vurdering av Ex-sone

- Sone 0: Alltid eksplosiv atmosfære, for eksempel inne i tanker med gass, brennbar væske. *Vurdering*: Trykksatte tanker og rørlinjer, samt produkttanker med brennbar væske (her: metanol) er ikke eksponert for antenningskilder
- Sone 1: Primær sone, tidvis eksplosiv atmosfære for eksempel fylle/tappe punkt *Vurdering*: Forsøksriggen er plassert inne i kabinett utstyrt med gassdetektorer for CO og hydrokarboner. Evt. lekkasjer/utslipp av brennbar gass/væske i forbindelse med tapping av metanol vil detekteres.
- Sone 2: Sekundert utslippssted, kan få eksplosiv atmosfære ved uhell, for eksempel ved flenser, ventiler og koblingspunkt *Vurdering*: Som i Sone 1: Gassdetektorer i kabinettet vil detektere utslipp av brennbar gass/væske

Samlet vurdering: Ut fra ovennevnte vurdering og funn ansees det ikke nødvendig å utstyre anlegget med Ex sikkert utstyr.

7.2 Trykkbeholdere

Forsøksriggen trykk- og lekkasjetestes rutinemessig foran hvert forsøk. Dokumenteres i lab-journal.

7.3 Påvirking av ytre miljø

Eksperimentene vil medføre mindre utslipp av hydrogen og karbonmonoksid, normalt i størrelsesorden 100-500 nml/min, maksimalt 1500 nml/min. Utslipp fra forsøksrigg føres over tak i egen, egnet ventilasjonskanal. DME foreligger i gassform ved romtemperatur og atmosfærisk trykk, og slippes derfor også ut. DME er brennbar, med IKKE giftig, carcinogen eller teratogen.

7.4 Bruk og behandling av kjemikalier

I forsøksriggen benyttes det ikke kjemikalier. Det produseres små mengder metanol (inntil 50 g metanol/døgn) i eksperimentene. Metanol avhendes ved NTNU Institutt for Kjemisk Prosessteknologi i henhold til egne rutiner (leveres til Arne Fossum)

7.5 Risikovurderingens metode

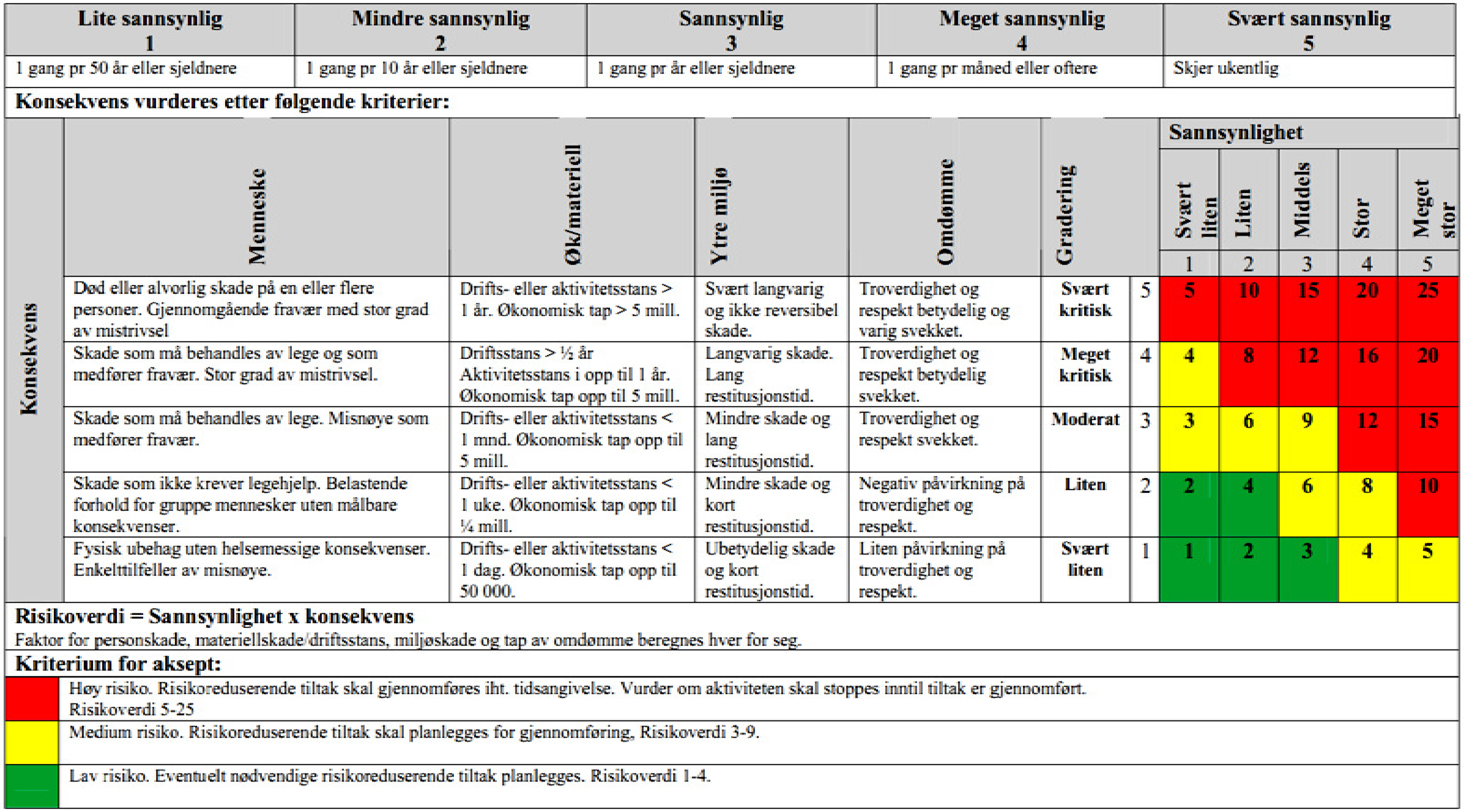
Risikovurderingen ble utført i følge NTNU/SINTEF Standard prosedyre for risikovurdering, med siktepunkt normal operasjonsprosedyrer for riggen.
Metoden er beskrevet i Tabell I. Funn i risikovurderingen er listet i Tabell II.

Det er fokusert på:

1. Hindre skader på personer
2. Hindre lekkasjer og utslipp som kan medføre brann og eller eksplosjon eller spredning av giftig gass eller kjemikalier
3. Skadebegrensning med tanke på materielle verdier
4. Utslipp til ytre miljø
5. Tap av omdømme

7.6 Risikovurdering matrise

Tabell I. Kategorisering av risikovurdering



Lite sannsynlig 1	Mindre sannsynlig 2	Sannsynlig 3	Meget sannsynlig 4	Svært sannsynlig 5
1 gang pr 50 år eller sjeldnere	1 gang pr 10 år eller sjeldnere	1 gang pr år eller sjeldnere	1 gang pr måned eller oftere	Skjer ukentlig

Konsekvens vurderes etter følgende kriterier:

Konsekvens	Menneske	Øk/materiell	Ytre miljø	Omdømme	Gradering		Sannsynlighet Svært liten 1	Liten 2	Middels 3	Stor 4	Meget stor 5
	Død eller alvorlig skade på en eller flere personer. Gjennomgående fravær med stor grad av mistrivsel	Drifts- eller aktivitetsstans > 1 år. Økonomisk tap > 5 mill.	Svært langvarig og ikke reversibel skade.	Troverdighet og respekt betydelig og varig svekket.	**Svært kritisk**	5	🟥 **5**	🟥 **10**	🟥 **15**	🟥 **20**	🟥 **25**
	Skade som må behandles av lege og som medfører fravær. Stor grad av mistrivsel.	Driftsstans > ½ år Aktivitetsstans i opp til 1 år. Økonomisk tap opp til 5 mill.	Langvarig skade. Lang restitusjonstid.	Troverdighet og respekt betydelig svekket.	**Meget kritisk**	4	🟨 **4**	🟥 **8**	🟥 **12**	🟥 **16**	🟥 **20**
	Skade som må behandles av lege. Misnøye som medfører fravær.	Drifts- eller aktivitetsstans < 1 mnd. Økonomisk tap opp til 5 mill.	Mindre skade og lang restitusjonstid.	Troverdighet og respekt svekket.	**Moderat**	3	🟨 **3**	🟨 **6**	🟨 **9**	🟥 **12**	🟥 **15**
	Skade som ikke krever legehjelp. Belastende forhold for gruppe mennesker uten målbare konsekvenser.	Drifts- eller aktivitetsstans < 1 uke. Økonomisk tap opp til ¼ mill.	Mindre skade og kort restitusjonstid.	Negativ påvirkning på troverdighet og respekt.	**Liten**	2	🟩 **2**	🟩 **4**	🟨 **6**	🟨 **8**	🟥 **10**
	Fysisk ubehag uten helsemessige konsekvenser. Enkelttilfeller av misnøye.	Drifts- eller aktivitetsstans < 1 dag. Økonomisk tap opp til 50 000.	Ubetydelig skade og kort restitusjonstid.	Liten påvirkning på troverdighet og respekt.	**Svært liten**	1	🟩 **1**	🟩 **2**	🟩 **3**	🟨 **4**	🟨 **5**

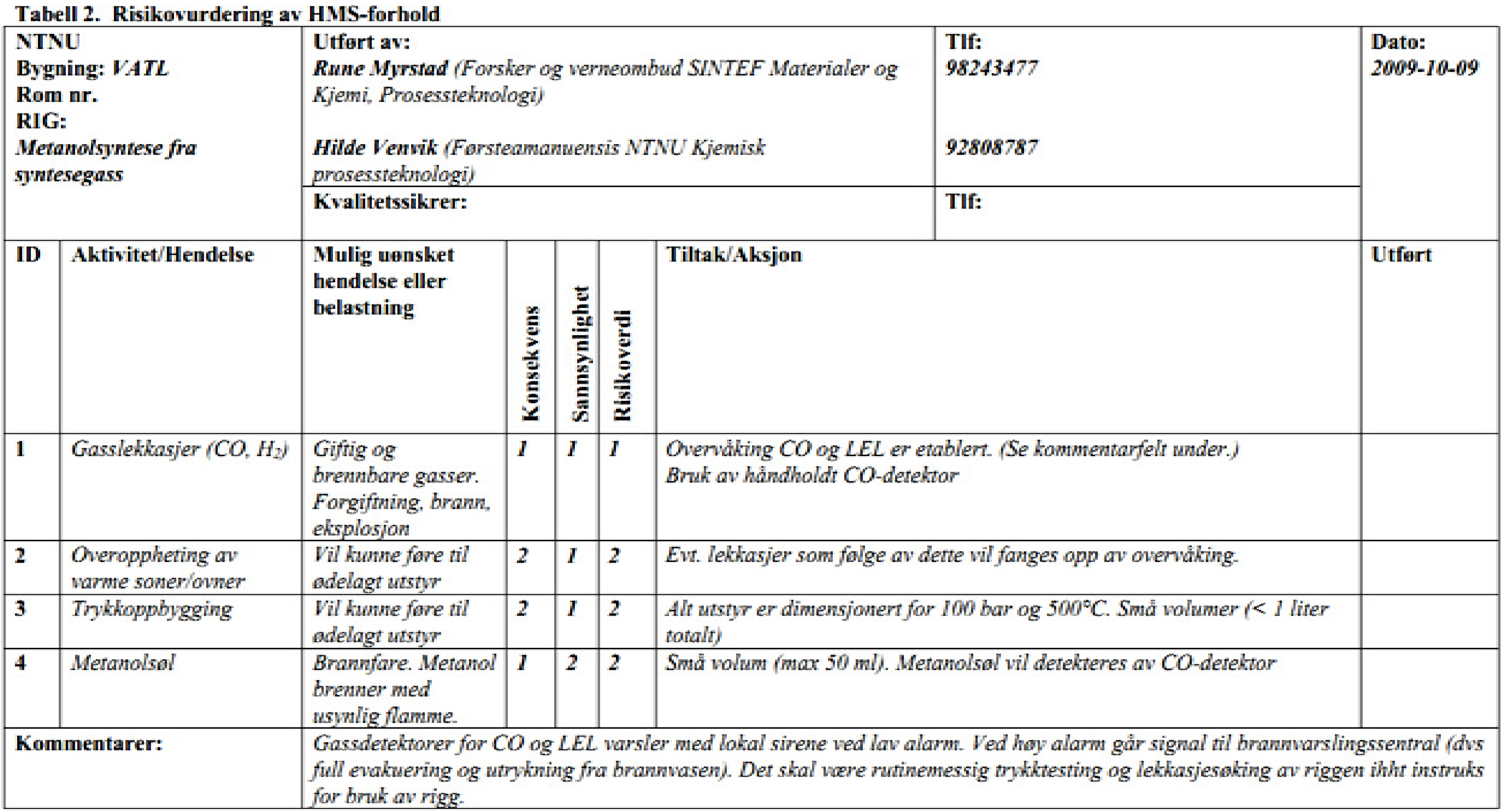
Risikoverdi = Sannsynlighet x konsekvens

Faktor for personskade, materiellskade/driftsstans, miljøskade og tap av omdømme beregnes hver for seg.

Kriterium for aksept:

🟥	Høy risiko. Risikoreduserende tiltak skal gjennomføres iht. tidsangivelse. Vurder om aktiviteten skal stoppes inntil tiltak er gjennomført. Risikoverdi 5-25
🟨	Medium risiko. Risikoreduserende tiltak skal planlegges for gjennomføring. Risikoverdi 3-9.
🟩	Lav risiko. Eventuelt nødvendige risikoreduserende tiltak planlegges. Risikoverdi 1-4.

APPENDIX J: RISK ASSESSMENT

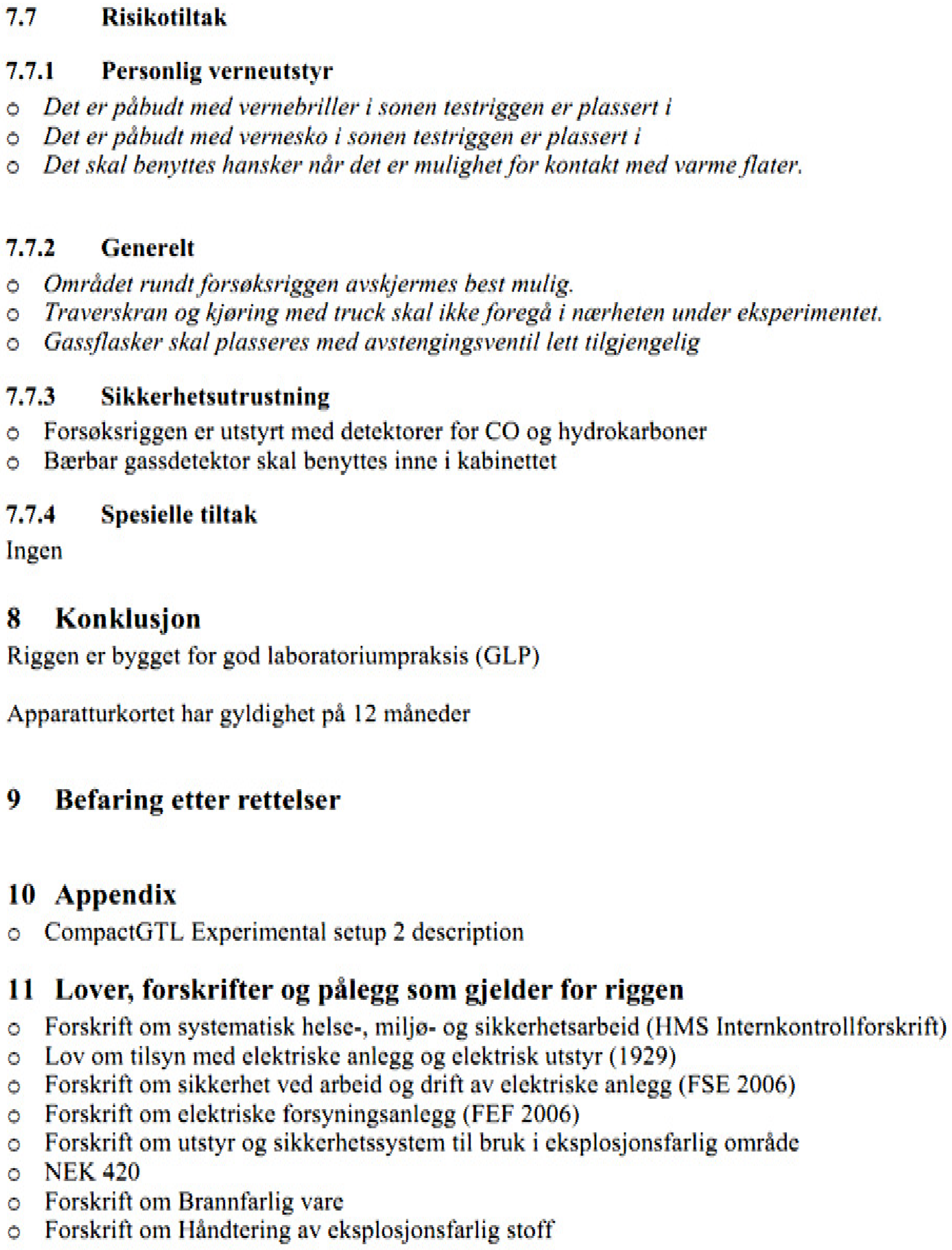


Tabell 2. Risikovurdering av HMS-forhold

NTNU **Bygning:** ***VATL*** **Rom nr.** **RIG:** ***Metanolsyntese fra syntesegass***	**Utført av:** ***Rune Myrstad*** *(Forsker og verneombud SINTEF Materialer og Kjemi, Prosessteknologi)* ***Hilde Venvik*** *(Førsteamanuensis NTNU Kjemisk prosessteknologi)*	**Tlf:** ***98243477*** ***92808787***	**Dato:** ***2009-10-09***
	Kvalitetssikrer:	**Tlf:**	

ID	**Aktivitet/Hendelse**	**Mulig uønsket hendelse eller belastning**	**Konsekvens**	**Sannsynlighet**	**Risikoverdi**	**Tiltak/Aksjon**	**Utført**
1	*Gasslekkasjer (CO, H_2)*	*Giftig og brennbare gasser. Forgiftning, brann, eksplosjon*	*1*	*1*	*1*	*Overvåking CO og LEL er etablert. (Se kommentarfelt under.)* *Bruk av håndholdt CO-detektor*	
2	*Overoppheting av varme soner/ovner*	*Vil kunne føre til ødelagt utstyr*	*2*	*1*	*2*	*Evt. lekkasjer som følge av dette vil fanges opp av overvåking.*	
3	*Trykkoppbygging*	*Vil kunne føre til ødelagt utstyr*	*2*	*1*	*2*	*Alt utstyr er dimensjonert for 100 bar og 500°C. Små volumer (< 1 liter totalt)*	
4	*Metanolsøl*	*Brannfare. Metanol brenner med usynlig flamme.*	*1*	*2*	*2*	*Små volum (max 50 ml). Metanolsøl vil detekteres av CO-detektor*	

Kommentarer: *Gassdetektorer for CO og LEL varsler med lokal sirene ved lav alarm. Ved høy alarm går signal til brannvarslingssentral (dvs full evakuering og utrykning fra brannvasen). Det skal være rutinemessig trykktesting og lekkasjesøking av riggen ihht instruks for bruk av rigg.*



7.7 Risikotiltak

7.7.1 Personlig verneutstyr

- *Det er påbudt med vernebriller i sonen testriggen er plassert i*
- *Det er påbudt med vernesko i sonen testriggen er plassert i*
- *Det skal benyttes hansker når det er mulighet for kontakt med varme flater.*

7.7.2 Generelt

- *Området rundt forsøksriggen avskjermes best mulig.*
- *Traverskran og kjøring med truck skal ikke foregå i nærheten under eksperimentet.*
- *Gassflasker skal plasseres med avstengingsventil lett tilgjengelig*

7.7.3 Sikkerhetsutrustning

- Forsøksriggen er utstyrt med detektorer for CO og hydrokarboner
- Bærbar gassdetektor skal benyttes inne i kabinettet

7.7.4 Spesielle tiltak

Ingen

8 Konklusjon

Riggen er bygget for god laboratoriumpraksis (GLP)

Apparaturkortet har gyldighet på 12 måneder

9 Befaring etter rettelser

10 Appendix

- CompactGTL Experimental setup 2 description

11 Lover, forskrifter og pålegg som gjelder for riggen

- Forskrift om systematisk helse-, miljø- og sikkerhetsarbeid (HMS Internkontrollforskrift)
- Lov om tilsyn med elektriske anlegg og elektrisk utstyr (1929)
- Forskrift om sikkerhet ved arbeid og drift av elektriske anlegg (FSE 2006)
- Forskrift om elektriske forsyningsanlegg (FEF 2006)
- Forskrift om utstyr og sikkerhetssystem til bruk i eksplosjonsfarlig område
- NEK 420
- Forskrift om Brannfarlig vare
- Forskrift om Håndtering av eksplosjonsfarlig stoff

Unit: **DME Synthesis Set-up** **Date: 10.12.2010**

Line manager:

Participants in the risk assessment (including their function):

Activity from the identification process form	**Potential undesirable incident/strain**	**LIKELIHOOD**	**CONSEQUENCE**			**Risk value**	**Comments/status Suggested measures**
		Likelihood (1-4)	Human (1-4)	Environment (1-4)	Economy/ materiel (1-4)		
Inert gases *Gases under pressure*	Pressure release Depletion	1	3	1	1		See *Hazardous Activity Identification Process*
Toxic gases (CO)	Inhalation	1	4	1	1		See *Hazardous Activity Identification Process*
Combustable gases (H_2,CO,CH_4)	Explosion Fire	1	3-4	1	3		See *Hazardous Activity Identification Process*
Mechanical work *Parts falling*	Blow	2-3	1-2	1	1		See *Hazardous Activity Identification Process* Fence(was installed)
Handeling and sythesis of Catalyst	Chemical exposure Toxicity/Sensitizing	2-3	1-2	1	1		See *Hazardous Activity Identification Process*
Activities around the rig at VTL	Explosion Fire	1	3-4	1	3		See *Hazardous Activity Identification Process*
Cleaning	Chemical exposure	1	1-2	1	1		See *Hazardous Activity Identification Process*

Likelihood, e.g.:

1. *Minimal*
2. *Low*
3. *High*
4. *Very high*

Consequence, e.g.:

1. *Relatively safe*
2. *Dangerous*
3. *Critical*
4. *Very critical*

Risk value (each one to be estimated separately):
Human = Likelihood x Human Consequence
Environmental = Likelihood x Environmental consequence
Financial/material = Likelihood x Consequence for Economy/materiel

NTNU	Hazardous Activity Identification Process	Prepared by	Number	Date
		The HSE section	HMSRV-12/24	01.12.2006
		Approved by	Page	Replaces
HSE		The Rector	39 of 168	20.08.1999

Unit: DME Synthesis Set-up **Date: 10.12.2010**

Participants in the identification process (including their function): Ayob Esmaelpour

Short description of the main activity/main process: Direct DME synthesis

Activity/process	Responsible person	Laws, regulations etc.	Existing documentation	Existing safety measures	Comment
Transport and mounting of gas bottles	Erik langørgen	NTNU HES Handbook	Safety data sheets	Gas alams, Transport vehicle,safety goggles	Pressure(200 bars) Toxic gases Combustable gases
Modification and maintenance of exprimental set-up	Rune Myrstad (SINTEF)	NTNU HES Handbook, Arbeidsmiljøloven	Safety data sheets, Risk assesment of set-up	Goggles	Pressure(70 bars) Toxic gases Combustable gases, Mechanical work
Leak testing and reactor installing	Fatemeh Hayer	NTNU HES Handbook, Arbeidsmiljøloven	Safety data sheets, DME set-up manual	Gas alams, goggles, Ventilation, Emergency stop device	Pressure(70 bars) Combustable gases, Mechanical work
Reaction experiment	Fatemeh Hayer	NTNU HES Handbook, Arbeidsmiljøloven	Safety data sheets	Gas alams, goggles, Ventilation	Pressure, Temperature and sample collection
Experiment shutdown and uninstalling of reactor	Fatemeh Hayer	NTNU HES Handbook, Arbeidsmiljøloven		Gas alams, goggles, Ventilation	
Cleaning of reactor	Ayob Esmaelpour		Safety data sheet	Goggles, gloves	
Handing of catalyst	Ayob Esmaelpour		Safety data sheet	Goggles, gloves	
Catalyst Synthesis	Karin Dragster		Safety data sheet	Goggles, gloves, Ventilation	
Working at VTL	Morten Grønli			Noise protection, activity monitoring, information, New fence	Risk of parts falling, other Exp. in VTL

NTNU	**HSE action plan**	Prepared by	Number	Date
		The HSE section	HMSRV-12/24	01.12.2006
		Approved by	Page	Replaces
HSE		The Rector	1 of 168	20.08.1999

Unit: **DME Synthesis Set-up**

What	Measure	Unit responsible	Priority	Cost	Current status
A fence was installed beside the DME synthesis set-up	To prevent the tools and materials from falling	Fatemeh Hayer			

J SAFETY DATA SHEETS

In accordance to regulations on classification, labelling etc., of dangerous chemicals and regulation on preparation and distribution of health, environment- and safety datasheet for dangerous chemicals.

YARA YARAPRAXAIR

SAFETY DATA SHEET

HYDROGEN (COMPRESSED)

1. Identification of the substance/preparation and of the company/undertaking

Identification of the substance or preparation

Product name : **HYDROGEN (COMPRESSED)**
Chemical name : Hydrogen
Chemical formula : H_2
Product registration number : 100254

Company/undertaking identification

Manufacturer / Supplier : Yara Praxair AS
P.O.Box 23 Haugenstua
N-0915 Oslo
Norway
T: +47 24 15 76 00
F: +47 24 15 75 50

e-mail address of person responsible for this SDS : industrial.no@yara.com

Emergency telephone number : **+47 48 005 000**

2 . Hazards identification

The product is classified as dangerous according to Directive 67/548/EEC and its amendments.

Classification : F+; R12
Physical/chemical hazards : Extremely flammable.

See section 11 for more detailed information on health effects and symptoms.

3 . Composition/information on ingredients

Substance/preparation : Substance

Ingredient name	CAS number	%	EC number	Classification
Hydrogen **See section 16 for the full text of the R-phrases declared above**	1333-74-0	100	215-605-7	F+; R12

There are no additional ingredients present which, within the current knowledge of the supplier and in the concentrations applicable, are classified as hazardous to health or the environment and hence require reporting in this section.

[1] Substance classified with a health or environmental hazard

[2] Substance with a workplace exposure limit

Occupational exposure limits, if available, are listed in section 8.

4. First-aid measures

Inhalation : Inhalation of vapours may cause dizziness, an irregular heartbeat, narcosis, nausea or asphyxiation. If inhaled, remove to fresh air.
Ingestion : No known effect according to our database.
Skin Contact : To avoid the risk of static discharges and gas ignition, soak contaminated clothing thoroughly with water before removing it. Not applicable (gas).
Eye contact : No known effect after eye contact. Rinse with water for a few minutes.

4. First-aid measures

Protection of first-aiders : No action shall be taken involving any personal risk or without suitable training. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation.

See section 11 for more detailed information on health effects and symptoms.

5. Fire-fighting measures

Extinguishing media : In case of fire, allow gas to burn if flow cannot be shut off immediately. Apply water from a safe distance to cool container and protect surrounding area.

Suitable : Use an extinguishing agent suitable for the surrounding fire.

Special exposure hazards : Flammable gas or vapour. Gas may accumulate in low or confined areas or travel a considerable distance to a source of ignition and flash back, causing fire or explosion.

Hazardous thermal decomposition products : No specific data.

Special protective equipment for fire-fighters : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

Remark : Container explosion may occur under fire conditions or when heated.

6. Accidental release measures

Personal precautions : Follow all fire-fighting procedures (section 5).

Environmental precautions and clean-up methods : Prevent entry into sewers, water courses, basements or confined areas. Exclude sources of ignition and ventilate the area.

Small spill : Immediately contact emergency personnel. Stop leak if without risk. Use spark-proof tools and explosion-proof equipment.

Note: see section 8 for personal protective equipment and section 13 for waste disposal.

7. Handling and storage

Handling : Keep container closed. Use only with adequate ventilation. Keep away from heat, sparks and flame. To avoid fire, eliminate ignition sources. Use explosion-proof electrical (ventilating, lighting and material handling) equipment. Take precautionary measures against static discharges.

Storage : Store in a segregated and approved area. Store in original container and secure against falling. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Store below 50 °C. Avoid all possible sources of ignition (spark or flame). Segregate from oxidising materials.

Packaging materials

Recommended : Use original container.

8. Exposure controls/personal protection

Ingredient name	Occupational exposure limits
Not available.	Simple asphyxiant.

Exposure controls

Respiratory protection : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.

Hand protection : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.

Eye protection : Recommended: safety glasses with side-shields

Skin protection : Personal protective equipment for the body should be selected based on the task being performed and the risks involved.

8. Exposure controls/personal protection

Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Ensure that eyewash stations and safety showers are close to the workstation location

9. Physical and chemical properties

General information

Appearance

Physical state : Gas. [Compressed gas]
Colour : Colourless.
Odour : Odourless.

Important health, safety and environmental information

Boiling point : -253,15°C (-423,7°F)
Melting/freezing point : -259.15°C (-434.5°F)
Flammability (solid, gas) : Extremely flammable gas.
Explosion Limits : Lower: 4% Upper: 77%
Density g/cm^3 : 0.071 g/cm^3
Solubility : Very slightly soluble in the following materials: cold water
Vapour density : 0.07 (Air = 1)
Critical temperature : -240.1°C (-400.2°F)

Other information

Auto-ignition temperature : 399.85 to 573.75°C (751.7 to 1064.8°F)

10. Stability and reactivity

Stability : Stable under recommended storage and handling conditions (see section 7).
Conditions to avoid : Avoid all possible sources of ignition (spark or flame). Do not pressurise, cut, weld, braze, solder, drill, grind or expose containers to heat or sources of ignition.
Materials to avoid : Reactive or incompatible with the following materials: oxidizing materials.
Hazardous decomposition products : No specific data.

11. Toxicological information

Potential acute health effects

Adverse health effects are considered unlikely, when the product is used according to directions.

Chronic effects : No known significant effects or critical hazards.
Carcinogenicity : No known significant effects or critical hazards.
Mutagenicity : No known significant effects or critical hazards.
Teratogenicity : No known significant effects or critical hazards.
Developmental effects : No known significant effects or critical hazards.
Fertility effects : No known significant effects or critical hazards.
Inhalation : No specific data.
Ingestion : No specific data.
Skin : No specific data.
Eyes : No specific data.

12. Ecological information

Environmental effects : No known significant effects or critical hazards.

Other adverse effects : No known significant effects or critical hazards.

13. Disposal considerations

Methods of disposal : Do not puncture or incinerate container. Dispose of in accordance with all applicable local and national regulations

European waste catalogue (EWC) : 16 05 04* gases in pressure containers (including halons) containing dangerous substances

Hazardous waste : This material and its container must be disposed of as hazardous waste.

Waste number : 7055

14. Transport information

International transport regulations

Regulatory information	UN number	Proper shipping name	Class	Packing group	Label	Additional information
ADR/RID Class	UN1049	HYDROGEN, COMPRESSED	2	-		**Hazard identification number** 23 **Limited quantity** LQ0 **CEFIC Tremcard** 20S1049
IMDG Class	UN1049	HYDROGEN, COMPRESSED	2.1	-		**Emergency schedules (EmS)** F-D; S-U
IATA-DGR Class	UN1049	HYDROGEN, COMPRESSED	2.1	-		**Passenger and Cargo Aircraft** Quantity limitation: 0 Forbidden **Cargo Aircraft Only** Quantity limitation: 150 kg

15. Regulatory information

EU regulations

Product use : Industrial applications.

Classification and labelling have been performed according to EU Directives 67/548/EEC and 1999/45/EC (including amendments) and the intended use.

Europe inventory : **Europe inventory:** This material is listed or exempted.

National regulations

Hazard symbol or symbols :

Extremely flammable

Risk phrases : R12- Extremely flammable.

Safety phrases : S9- Keep container in a well-ventilated place.
S16- Keep away from sources of ignition - No smoking.
S33- Take precautionary measures against static discharges.

Carcinogenic class : Not classified.

Contains EINECS number : Hydrogen 215-605-7

16. Other information

Full text of R-phrases referred to in sections 2 and 3 - Norway	: ◤R12- Extremely flammable.
Full text of classifications referred to in sections 2 and 3 - Norway	: ◤F+ - Extremely flammable
References	: European Chemical Bureau, Annex 1 EU Directive 67/548/EEC National Institute for Occupational Safety and Health, U.S. Dept. of Health, Education, and Welfare, Reports and Memoranda Registry of Toxic Effects of Chemical Substances Atrion International Inc. 4777 Levy Street, St Laurent, Quebec HAR 2P9, Canada

History

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Date of previous issue	: **03.11.2005.**
Version	: **3**
Prepared by	: Yara Product Classification and Regulations

◤ **Indicates information that has changed from previously issued version.**

Notice to reader

To the best of our knowledge, the information provided in this Safety Data Sheet is accurate as at the date of its issue. The information it contains is being given for safety guidance purposes and relates only to the specific material and uses described in it. This information does not necessarily apply to that material when combined with other material(s) or when used otherwise than as described herein. Final determination of the suitability of any material is the sole responsibility of the user. All materials may represent unknown hazards and should be used with caution. Yara International ASA disclaims any liability for loss or damage resulting from the use of any data, information or recommendations set out in this Safety Data Sheet.

In accordance to regulations on classification, labelling etc., of dangerous chemicals and regulation on preparation and distribution of health, environment- and safety datasheet for dangerous chemicals.

YARA YARAPRAXAIR

SAFETY DATA SHEET

CARBON MONOXIDE

1. Identification of the substance/preparation and of the company/undertaking

Identification of the substance or preparation

Product name	:	**CARBON MONOXIDE**
Chemical name	:	Carbon monoxide
Synonyms	:	carbone (oxyde de) (french); carbonic oxide; carbonio (ossido di) (italian); carbon monoxide ; carbon oxide (co); exhaust gas; flue gas; kohlenmonoxid (german); koolmonoxyde (dutch); oxyde de carbone (french); wegla tlenek (polish)
Chemical formula	:	C-O
Product registration number	:	05962

Company/undertaking identification

Manufacturer / Supplier :

Yara Praxair AS
P.O.Box 23 Haugenstua
N-0915 Oslo
Norway
T: +47 24 15 76 00
F: +47 24 15 75 50

e-mail address of person responsible for this SDS : industrial.no@yara.com

Emergency telephone number : **+47 48 005 000**

2 . Hazards identification

The product is classified as dangerous according to Directive 67/548/EEC and its amendments.

Classification :

F+; R12
Repr. Cat. 1; R61
T; R23, R48/23

Physical/chemical hazards : Extremely flammable.

Human health hazards : May cause harm to the unborn child. Also toxic by inhalation. Also toxic: danger of serious damage to health by prolonged exposure through inhalation.

See section 11 for more detailed information on health effects and symptoms.

3 . Composition/information on ingredients

Substance/preparation : Substance

Ingredient name	**CAS number**	**%**	**EC number**	**Classification**	
Carbon monoxide **See section 16 for the full text of the R-phrases declared above**	630-08-0	100	211-128-3	F+; R12 Repr. Cat. 1; R61 T; R23, R48/23	[1] [2]

There are no additional ingredients present which, within the current knowledge of the supplier and in the concentrations applicable, are classified as hazardous to health or the environment and hence require reporting in this section.

[1] Substance classified with a health or environmental hazard

[2] Substance with a workplace exposure limit

3 . Composition/information on ingredients

Occupational exposure limits, if available, are listed in section 8.

4. First-aid measures

Inhalation : If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Ingestion : Not applicable

Skin Contact : To avoid the risk of static discharges and gas ignition, soak contaminated clothing thoroughly with water before removing it. Continue to rinse for at least 10 minutes. Get medical attention. Not applicable (gas).

Eye contact : Not applicable

Protection of first-aiders : No action shall be taken involving any personal risk or without suitable training. If it is suspected that fumes are still present, the rescuer should wear an appropriate mask or self-contained breathing apparatus. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation. Wash contaminated clothing thoroughly with water before removing it, or wear gloves.

See section 11 for more detailed information on health effects and symptoms.

5. Fire-fighting measures

Extinguishing media : In case of fire, allow gas to burn if flow cannot be shut off immediately. Apply water from a safe distance to cool container and protect surrounding area.

Suitable : Use an extinguishing agent suitable for the surrounding fire.

Special exposure hazards : Flammable gas or vapour. Gas may accumulate in low or confined areas or travel a considerable distance to a source of ignition and flash back, causing fire or explosion.

Hazardous thermal decomposition products : These products are
carbon dioxide
carbon monoxide

Special protective equipment for fire-fighters : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

6. Accidental release measures

Personal precautions : Follow all fire-fighting procedures (section 5).

Small spill : Immediately contact emergency personnel. Stop leak if without risk. Use spark-proof tools and explosion-proof equipment.

Note: see section 8 for personal protective equipment and section 13 for waste disposal.

7. Handling and storage

Handling : Use only in well-ventilated areas. Keep container closed. Acts as a simple asphyxiant. Can displace the normal air and cause suffocation from lack of oxygen. Inhalation may cause headaches, dizziness, drowsiness, and nausea. See section 11 for more detailed information on health effects and symptoms.

Storage : Store in a segregated and approved area. Store in original container and secure against falling. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame). Segregate from oxidising materials.

Packaging materials

Recommended : Use original container.

8. Exposure controls/personal protection

Ingredient name	Occupational exposure limits
Carbon monoxide	**Arbeidstilsynet (Norway, 6/2007).** (15-min TWA): 100 ppm 15 minute(s). TWA: 29 mg/m³ 8 hour(s). TWA: 25 ppm 8 hour(s).

Exposure controls

Respiratory protection : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.
Recommended: self-contained breathing apparatus (SCBA)

Hand protection : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.

Skin protection : Personal protective equipment for the body should be selected based on the task being performed and the risks involved.

Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Ensure that eyewash stations and safety showers are close to the workstation location

9. Physical and chemical properties

General information

Appearance

Physical state : Gas.

Colour : Colourless.

Odour : Odourless.

Important health, safety and environmental information

Boiling point : -191,66°C (-313°F)

Melting/freezing point : -198.88°C (-326°F)

Flammability (solid, gas) : Extremely flammable gas.

Explosion Limits : Lower: 12.5% Upper: 74.2%

Density g/cm^3 : 0.0012 g/cm^3 (15°C / 59°F)

Solubility : Very slightly soluble in the following materials: cold water

Viscosity : Dynamic: 0,01657 mPa·s (0,01657 cP)

Vapour density : 0.97 (Air = 1)

Critical temperature : -140.1°C (-220.2°F)

Other information

Auto-ignition temperature : 608.89°C (1128°F)

10. Stability and reactivity

Stability : Stable under recommended storage and handling conditions (see section 7).

Conditions to avoid : Avoid all possible sources of ignition (spark or flame). Do not pressurise, cut, weld, braze, solder, drill, grind or expose containers to heat or sources of ignition. Avoid exposure - obtain special instructions before use. Avoid exposure during pregnancy.

Materials to avoid : Reactive or incompatible with the following materials: oxidizing materials and combustible materials.

Hazardous decomposition products : These products are
carbon dioxide
carbon monoxide

11. Toxicological information

Potential acute health effects

Inhalation : Toxic by inhalation.

Skin Contact : Adverse health effects are considered unlikely, when the product is used according to directions.

Eye contact : Adverse health effects are considered unlikely, when the product is used according to directions.

Product/ingredient name	Result	Species	Dose	Exposure	References
Carbon monoxide	TDLo Intraperitoneal	Rat	35 mL/kg	-	NETEEC 23,157,2001

Chronic effects : Toxic: danger of serious damage to health by prolonged exposure through inhalation.

Carcinogenicity : No known significant effects or critical hazards.

Mutagenicity : No known significant effects or critical hazards.

Teratogenicity : Can cause birth defects.

Developmental effects : No known significant effects or critical hazards.

Fertility effects : No known significant effects or critical hazards.

Inhalation : No specific data.

Ingestion : No specific data.

Skin : No specific data.

Eyes : No specific data.

Target organs : Causes damage to the following organs: blood, lungs, cardiovascular system, central nervous system (CNS).

12. Ecological information

Environmental effects : No known significant effects or critical hazards.

Other adverse effects : No known significant effects or critical hazards.

13. Disposal considerations

Methods of disposal : Do not puncture or incinerate container. Dispose of in accordance with all applicable local and national regulations

European waste catalogue (EWC) : 16 05 04* gases in pressure containers (including halons) containing dangerous substances

Hazardous waste : This material and its container must be disposed of as hazardous waste.

Waste number : 7055

14. Transport information

International transport regulations

Regulatory information	UN number	Proper shipping name	Class	Packing group	Label	Additional information
ADR/RID Class	UN1016	CARBON MONOXIDE, COMPRESSED	2	-		**Hazard identification number** 263 **Limited quantity** LQ0 **CEFIC Tremcard** 20S1016

IMDG Class	UN1016	CARBON MONOXIDE, COMPRESSED	2.3	-		**Emergency schedules (EmS)** F-D; S-U
IATA-DGR Class	UN1016	CARBON MONOXIDE, COMPRESSED	2.3	-		**Passenger and Cargo Aircraft** Quantity limitation: 0 Forbidden **Cargo Aircraft Only**Quantity limitation: 25 kg

15. Regulatory information

EU regulations

Product use : Industrial applications.

Classification and labelling have been performed according to EU Directives 67/548/EEC and 1999/45/EC (including amendments) and the intended use.

Europe inventory : **Europe inventory:** This material is listed or exempted.

Restrictions on the Marketing and Use Directive : Restricted to professional users.

National regulations

Hazard symbol or symbols :

Extremely flammable, Toxic

Risk phrases :
R12- Extremely flammable.
R61- May cause harm to the unborn child.
R23- Also toxic by inhalation.
R48/23- Also toxic: danger of serious damage to health by prolonged exposure through inhalation.

Safety phrases :
S53- Avoid exposure - obtain special instructions before use.
S45- In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

Carcinogenic class : Not classified.

Contains EINECS number : Carbon monoxide 211-128-3

16. Other information

Full text of R-phrases referred to in sections 2 and 3 - Norway :
R12- Extremely flammable.
R61- May cause harm to the unborn child.
R23- Also toxic by inhalation.
R48/23- Also toxic: danger of serious damage to health by prolonged exposure through inhalation.

Full text of classifications referred to in sections 2 and 3 - Norway :
F+ - Extremely flammable
Repr. Cat. 1 - Toxic to reproduction Category 1
T - Toxic

References :
European Chemical Bureau, Annex 1 EU Directive 67/548/EEC
National Institute for Occupational Safety and Health, U.S. Dept. of Health, Education, and Welfare, Reports and Memoranda
Registry of Toxic Effects of Chemical Substances
Atrion International Inc. 4777 Levy Street, St Laurent, Quebec HAR 2P9, Canada

16. Other information

History

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Prepared by : Yara Product Classification and Regulations

◤ **Indicates information that has changed from previously issued version.**

Notice to reader

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In accordance to regulations on classification, labelling etc., of dangerous chemicals and regulation on preparation and distribution of health, environment- and safety datasheet for dangerous chemicals.

YARA YARAPRAXAIR

SAFETY DATA SHEET

CARBON DIOXIDE (COMPRESSED)

1. Identification of the substance/preparation and of the company/undertaking

Identification of the substance or preparation

Product name : **CARBON DIOXIDE (COMPRESSED)**

Chemical name : carbon dioxide

Synonyms : anhydride carbonique (french); carbonic acid gas; carbonic anhydride; kohlensaure (german)

Chemical formula : CO_2

Company/undertaking identification

Manufacturer / Supplier :
Yara Praxair AS
P.O.Box 23 Haugenstua
N-0915 Oslo
Norway
T: +47 24 15 76 00
F: +47 24 15 75 50

e-mail address of person responsible for this SDS : industrial.no@yara.com

Emergency telephone number : **+47 48 005 000**

2 . Hazards identification

The product is not classified as dangerous according to Directive 67/548/EEC and its amendments.

Classification : Not classified.

Additional hazards : Acts as a simple asphyxiant. The vapour/gas is heavier than air and will spread along the ground.

See section 11 for more detailed information on health effects and symptoms.

3 . Composition/information on ingredients

Substance/preparation : Substance

Ingredient name	CAS number	%	EC number	Classification
carbon dioxide **See section 16 for the full text of the R-phrases declared above**	124-38-9	100	204-696-9	Not classified. [2]

There are no additional ingredients present which, within the current knowledge of the supplier and in the concentrations applicable, are classified as hazardous to health or the environment and hence require reporting in this section.

[1] Substance classified with a health or environmental hazard

[2] Substance with a workplace exposure limit

Occupational exposure limits, if available, are listed in section 8.

4. First-aid measures

Inhalation	If inhaled, remove to fresh air. If breathing is difficult, give oxygen. In all cases of doubt, or when symptoms persist, seek medical attention.
Ingestion	Not applicable
Skin Contact	Not applicable (gas).
Eye contact	Not applicable
Protection of first-aiders	No action shall be taken involving any personal risk or without suitable training.

See section 11 for more detailed information on health effects and symptoms.

5. Fire-fighting measures

Extinguishing media	The product itself has fire-extinguishing properties.
Suitable	Use an extinguishing agent suitable for the surrounding fire.
Special exposure hazards	Container explosion may occur under fire conditions or when heated.
Hazardous thermal decomposition products	These products are carbon dioxide carbon monoxide
Special protective equipment for fire-fighters	Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

6. Accidental release measures

Personal precautions	Follow all fire-fighting procedures (section 5).
Small spill	Immediately contact emergency personnel. Stop leak if without risk.

Note: see section 8 for personal protective equipment and section 13 for waste disposal.

7. Handling and storage

Handling	Use only in well-ventilated areas. Keep container closed. Acts as a simple asphyxiant. Can displace the normal air and cause suffocation from lack of oxygen. Inhalation may cause headaches, dizziness, drowsiness, and nausea. See section 11 for more detailed information on health effects and symptoms.
Storage	Store in a segregated and approved area. Store in original container and secure against falling.
Packaging materials	
Recommended	Use original container.
Specific uses	Liquid carbon dioxide (also valid for compressed carbon dioxide) must never be used to rinse tanks, containers or equipment containing flammable liquids/gases, particulates or dust. Risk of explosion in presence of static discharge. If carbon dioxide gas is used to rinse equipment, tanks or containers, take precautionary measures against static discharges.

8. Exposure controls/personal protection

Ingredient name	Occupational exposure limits
carbon dioxide	**Arbeidstilsynet (Norway, 6/2007).** TWA: 9000 mg/m^3 8 hour(s). TWA: 5000 ppm 8 hour(s).

Exposure controls	
Respiratory protection	Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator. Recommended: A respirator is not needed under normal and intended conditions of product use. The vapour/gas is heavier than air and will spread along the ground. In case of insufficient ventilation, wear suitable respiratory equipment.
Hand protection	Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.

8. Exposure controls/personal protection

Skin protection : Personal protective equipment for the body should be selected based on the task being performed and the risks involved.

Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Ensure that eyewash stations and safety showers are close to the workstation location

9. Physical and chemical properties

General information

Appearance

Physical state : Gas. [Compressed gas]

Colour : Colourless.

Odour : Odourless.

Important health, safety and environmental information

Boiling point : -78,55°C (-109,4°F)

Melting/freezing point : Sublimation temperature: -78.5°C (-109.3°F)

Density g/cm^3 : 0.0019 g/cm^3

Vapour density : 1.53 (Air = 1)

Critical temperature : 30.9°C (87.6°F)

10. Stability and reactivity

Stability : Stable under recommended storage and handling conditions (see section 7).

Hazardous decomposition products : These products are
carbon dioxide
carbon monoxide

11. Toxicological information

Potential acute health effects

Adverse health effects are considered unlikely, when the product is used according to directions.

Acute toxicity

Conclusion/Summary : Acts as a simple asphyxiant: Symptoms and signs include headache, dizziness, fatigue, drowsiness (between 4 and 5 vol%) and in extreme cases, loss of consciousness (between 6 and 8%). Potential suffocation hazard.

Chronic effects : No known significant effects or critical hazards.

Carcinogenicity : No known significant effects or critical hazards.

Mutagenicity : No known significant effects or critical hazards.

Teratogenicity : No known significant effects or critical hazards.

Developmental effects : No known significant effects or critical hazards.

Fertility effects : No known significant effects or critical hazards.

Inhalation : No specific data.

Ingestion : No specific data.

Skin : No specific data.

Eyes : No specific data.

Target organs : Causes damage to the following organs: lungs, cardiovascular system, skin, eyes, central nervous system (CNS), eye, lens or cornea.

12. Ecological information

Environmental effects : No known significant effects or critical hazards.

Other adverse effects : No known significant effects or critical hazards.

13. Disposal considerations

Methods of disposal : Do not puncture or incinerate container. Dispose of in accordance with all applicable local and national regulations

Hazardous waste : Within the present knowledge of the supplier, this product is not regarded as hazardous waste, as defined by EU Directive 91/689/EEC..

14. Transport information

International transport regulations

Regulatory information	UN number	Proper shipping name	Class	Packing group	Label	Additional information
ADR/RID Class	UN1013	CARBON DIOXIDE	2	-		**Hazard identification number** 20 **Limited quantity** LQ1 **CEFIC Tremcard** 20S1013
IMDG Class	UN1013	CARBON DIOXIDE	2.2	-		**Emergency schedules (EmS)** F-C; S-V
IATA-DGR Class	UN1013	CARBON DIOXIDE	2.2	-		**Passenger and Cargo Aircraft** Quantity limitation: 75 kg **Cargo Aircraft Only**Quantity limitation: 150 kg

15. Regulatory information

EU regulations

Product use : Industrial applications.

Classification and labelling have been performed according to EU Directives 67/548/EEC and 1999/45/EC (including amendments) and the intended use.

Europe inventory : **Europe inventory:** This material is listed or exempted.

Additional warning phrases : Safety data sheet available for professional user on request.

National regulations

Risk phrases : Not classified.

Carcinogenic class : Not classified.

16. Other information

References : European Chemical Bureau, Annex 1 EU Directive 67/548/EEC
National Institute for Occupational Safety and Health, U.S. Dept. of Health, Education, and Welfare, Reports and Memoranda
Registry of Toxic Effects of Chemical Substances
Atrion International Inc. 4777 Levy Street, St Laurent, Quebec HAR 2P9, Canada

History

Date of printing : **31.12.2007.**

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In accordance to regulations on classification, labelling etc., of dangerous chemicals and regulation on preparation and distribution of health, environment- and safety datasheet for dangerous chemicals.

YARA YARAPRAXAIR

SAFETY DATA SHEET

METHANE

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1. Identification of the substance/preparation and of the company/undertaking

Identification of the substance or preparation

Product name	: **METHANE**
Chemical name	: Methane
Synonyms	: fire damp; marsh gas; methane (dot); methyl hydride
Chemical formula	: C-H4

Company/undertaking identification

Manufacturer / Supplier :

Yara Praxair AS
P.O.Box 23 Haugenstua
N-0915 Oslo
Norway
T: +47 24 15 76 00
F: +47 24 15 75 50

e-mail address of person responsible for this SDS : industrial.no@yara.com

Emergency telephone number : **+47 48 005 000**

2 . Hazards identification

The product is classified as dangerous according to Directive 67/548/EEC and its amendments.

Classification : F+; R12

Physical/chemical hazards : Extremely flammable.

See section 11 for more detailed information on health effects and symptoms.

3 . Composition/information on ingredients

Substance/preparation : Substance

Ingredient name	CAS number	%	EC number	Classification
Methane **See section 16 for the full text of the R-phrases declared above**	74-82-8	100	200-812-7	F+; R12

There are no additional ingredients present which, within the current knowledge of the supplier and in the concentrations applicable, are classified as hazardous to health or the environment and hence require reporting in this section.

[1] Substance classified with a health or environmental hazard

[2] Substance with a workplace exposure limit

Occupational exposure limits, if available, are listed in section 8.

4. First-aid measures

Inhalation : If inhaled, remove to fresh air. If breathing is difficult, give oxygen. In all cases of doubt, or when symptoms persist, seek medical attention.

Ingestion : Not applicable

Skin Contact : To avoid the risk of static discharges and gas ignition, soak contaminated clothing thoroughly with water before removing it. Not applicable (gas).

Eye contact : Not applicable

4. First-aid measures

Protection of first-aiders : No action shall be taken involving any personal risk or without suitable training. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation.

See section 11 for more detailed information on health effects and symptoms.

5. Fire-fighting measures

Extinguishing media : In case of fire, allow gas to burn if flow cannot be shut off immediately. Apply water from a safe distance to cool container and protect surrounding area.

Suitable : Use an extinguishing agent suitable for the surrounding fire.

Special exposure hazards : Flammable gas or vapour. Gas may accumulate in low or confined areas or travel a considerable distance to a source of ignition and flash back, causing fire or explosion.

Hazardous thermal decomposition products : These products are
carbon dioxide
carbon monoxide

Special protective equipment for fire-fighters : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

6. Accidental release measures

Personal precautions : Follow all fire-fighting procedures (section 5).

Small spill : Immediately contact emergency personnel. Stop leak if without risk. Use spark-proof tools and explosion-proof equipment.

Note: see section 8 for personal protective equipment and section 13 for waste disposal.

7. Handling and storage

Handling : Use only in well-ventilated areas. Keep container closed. Acts as a simple asphyxiant. Can displace the normal air and cause suffocation from lack of oxygen. Inhalation may cause headaches, dizziness, drowsiness, and nausea. See section 11 for more detailed information on health effects and symptoms.

Storage : Store in a segregated and approved area. Store in original container and secure against falling. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame). Segregate from oxidising materials.

Packaging materials

Recommended : Use original container.

8. Exposure controls/personal protection

Ingredient name	Occupational exposure limits
Not available.	Simple asphyxiant.

Exposure controls

Respiratory protection : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.
Possible: supplied-air respirator

Hand protection : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.

Skin protection : Personal protective equipment for the body should be selected based on the task being performed and the risks involved.

Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Ensure that eyewash stations and safety showers are close to the workstation location

9. Physical and chemical properties

General information

Appearance

Physical state : Gas.

Colour : Colourless.

Odour : Sweetish. [Slight]

Important health, safety and environmental information

Boiling point : -161,55°C (-258,8°F)

Melting/freezing point : -182.6°C (-296.7°F)

Flash point : Closed cup: -188.15°C (-306.7°F).

Flammability (solid, gas) : Extremely flammable gas.

Explosion Limits : Lower: 5% Upper: 15%

Vapour density : 0.55 (Air = 1)

Critical temperature : -82.4°C (-116.3°F)

Other information

Auto-ignition temperature : 539.85°C (1003.7°F)

10. Stability and reactivity

Stability : Stable under recommended storage and handling conditions (see section 7).

Conditions to avoid : Avoid all possible sources of ignition (spark or flame). Do not pressurise, cut, weld, braze, solder, drill, grind or expose containers to heat or sources of ignition.

Hazardous decomposition products : These products are
carbon dioxide
carbon monoxide

11. Toxicological information

Potential acute health effects

Adverse health effects are considered unlikely, when the product is used according to directions.

Chronic effects : No known significant effects or critical hazards.

Carcinogenicity : No known significant effects or critical hazards.

Mutagenicity : No known significant effects or critical hazards.

Teratogenicity : No known significant effects or critical hazards.

Developmental effects : No known significant effects or critical hazards.

Fertility effects : No known significant effects or critical hazards.

Inhalation : No specific data.

Ingestion : No specific data.

Skin : No specific data.

Eyes : No specific data.

12. Ecological information

Environmental effects : No known significant effects or critical hazards.

Other adverse effects : No known significant effects or critical hazards.

13. Disposal considerations

Methods of disposal : Do not puncture or incinerate container. Dispose of in accordance with all applicable local and national regulations

European waste catalogue (EWC) : 16 05 04* gases in pressure containers (including halons) containing dangerous substances

Hazardous waste : This material and its container must be disposed of as hazardous waste.

Waste number : 7055

14. Transport information

International transport regulations

Regulatory information	UN number	Proper shipping name	Class	Packing group	Label	Additional information
ADR/RID Class	UN1971	METHANE, COMPRESSED	2	-		**Hazard identification number** 23
IMDG Class	UN1971	METHANE, COMPRESSED	2.1	-		**Emergency schedules (EmS)** F-D, S-U
IATA-DGR Class	UN1971	METHANE, COMPRESSED	2.1	-		**Passenger and Cargo Aircraft** Quantity limitation: 0 Forbidden **Cargo Aircraft Only**Quantity limitation: 150 kg

15. Regulatory information

EU regulations

Product use : Industrial applications.

Classification and labelling have been performed according to EU Directives 67/548/EEC and 1999/45/EC (including amendments) and the intended use.

Europe inventory : **Europe inventory:** This material is listed or exempted.

Other EU regulations

Tactile warning of danger : Yes, applicable.

National regulations

Hazard symbol or symbols :

Extremely flammable

Risk phrases : R12- Extremely flammable.

Safety phrases : S2- Keep out of the reach of children.
S9- Keep container in a well-ventilated place.
S16- Keep away from sources of ignition - No smoking.
S33- Take precautionary measures against static discharges.

Carcinogenic class : Not classified.

Contains EINECS number : Methane 200-812-7

16. Other information

Full text of R-phrases referred to in sections 2 and 3 - Norway : R12- Extremely flammable.

Full text of classifications referred to in sections 2 and 3 - Norway : F+ - Extremely flammable

References : European Chemical Bureau, Annex 1 EU Directive 67/548/EEC
National Institute for Occupational Safety and Health, U.S. Dept. of Health, Education, and Welfare, Reports and Memoranda
Registry of Toxic Effects of Chemical Substances
Atrion International Inc. 4777 Levy Street, St Laurent, Quebec HAR 2P9, Canada

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SAFETY DATA SHEET

METHANOL

1. Identification of the substance/preparation and of the company/undertaking

Identification of the substance or preparation

Product name : **METHANOL**

Chemical name : Methanol

Synonyms : alcool methylique (french); alcool metilico (italian); carbinol; colonial spirit; columbian spirit; columbian spirits (dot); methanol (dot); metanolo (italian); methyl alcohol; methyl alcohol (dot); methylol; methylalkohol (german); methyl hydroxide; metylowy alkohol (polish); monohydroxymethane; pyroxylic spirit; wood alcohol; wood naphtha; wood spirit

Chemical formula : C-H4-O

Product registration number : 056212

Company/undertaking identification

Manufacturer / Supplier :
Yara Norge AS
Industrial Products
P.O.Box 2464, Solli
N-0202 Oslo
Norway
T: +47 24 15 70 00
F: +47 24 15 72 10

e-mail address of person responsible for this SDS : Yara-kjemikalieordre@yara.com

Emergency telephone number : **+47 22 59 13 00 (Giftinformasjonen)**

2 . Hazards identification

The product is classified as dangerous according to Directive 67/548/EEC and its amendments.

Classification : F; R11
T; R23/24/25, R39/23/24/25

Physical/chemical hazards : Highly flammable.

Human health hazards : Toxic by inhalation, in contact with skin and if swallowed. Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.

See section 11 for more detailed information on health effects and symptoms.

3 . Composition/information on ingredients

Substance/preparation : Substance

Ingredient name	CAS number	%	EC number	Classification	
Methanol	67-56-1	100	200-659-6	F; R11 T; R23/24/25, R39/23/24/25	[1] [2]
See section 16 for the full text of the R-phrases declared above					

There are no additional ingredients present which, within the current knowledge of the supplier and in the concentrations applicable, are classified as hazardous to health or the environment and hence require reporting in this section.

[1] Substance classified with a health or environmental hazard

[2] Substance with a workplace exposure limit

3 . Composition/information on ingredients

Occupational exposure limits, if available, are listed in section 8.

4. First-aid measures

Inhalation : If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Ingestion : Do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Get medical attention immediately.

Skin Contact : Get medical attention immediately. Wash contaminated clothing thoroughly with water before removing it, or wear gloves. Continue to rinse for at least 10 minutes. Avoid prolonged or repeated contact with skin. Wash with soap and water.

Eye contact : In case of contact with eyes, rinse immediately with plenty of water. Get medical attention if irritation occurs.

Protection of first-aiders : No action shall be taken involving any personal risk or without suitable training. If it is suspected that fumes are still present, the rescuer should wear an appropriate mask or self-contained breathing apparatus. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation.

See section 11 for more detailed information on health effects and symptoms.

5. Fire-fighting measures

Extinguishing media : In case of fire, use water spray (fog), foam, dry chemical or CO_2.

Suitable : Use dry chemical, CO_2, water spray (fog) or foam.

Not suitable : Do not use water jet.

Special exposure hazards : Highly flammable liquid and vapour. Vapour may cause flash fire. Vapours may accumulate in low or confined areas or travel a considerable distance to a source of ignition and flash back. Runoff to sewer may create fire or explosion hazard.

Hazardous thermal decomposition products : These products are
carbon dioxide
carbon monoxide

Special protective equipment for fire-fighters : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

6. Accidental release measures

Personal precautions : Do not touch or walk through spilt material.

Environmental precautions and clean-up methods : Avoid contact of spilt material and runoff with soil and surface waterways.

If emergency personnel are unavailable, contain spilt material. For small spills, add absorbent (soil may be used in the absence of other suitable materials) and use a non-sparking or explosion-proof means to transfer material to a sealable, appropriate container for disposal. For large spills, dyke spilt material or otherwise contain material to ensure runoff does not reach a waterway. Place spilt material in an appropriate container for disposal.

Note: see section 8 for personal protective equipment and section 13 for waste disposal.

7. Handling and storage

Handling : Do not ingest. Avoid contact with eyes, skin and clothing. Keep container closed. Use only with adequate ventilation. Avoid breathing vapour or mist. Keep away from heat, sparks and flame. To avoid fire or explosion, dissipate static electricity during transfer by earthing and bonding containers and equipment before transferring material. Use explosion-proof electrical (ventilating, lighting and material handling) equipment. Wash thoroughly after handling.

Storage : Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).

Packaging materials

Recommended : Use original container.

8. Exposure controls/personal protection

Ingredient name	Occupational exposure limits
Methanol	**Arbeidstilsynet (Norway, 6/2007). Skin** TWA: 130 mg/m³ 8 hour(s). TWA: 100 ppm 8 hour(s).

Exposure controls

Respiratory protection : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.
Recommended: half-face mask , organic vapour filter (Type A)

Hand protection : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.
>8 hours (breakthrough time): butyl rubber, PTFE, Viton

Eye protection : Recommended: splash goggles
Possible: face shield

Skin protection : Personal protective equipment for the body should be selected based on the task being performed and the risks involved.
Recommended: overall, safety apron

Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Ensure that eyewash stations and safety showers are close to the workstation location

9. Physical and chemical properties

General information

Appearance

Physical state : Liquid. [Clear.]

Colour : Colourless.

Odour : Pungent. Sweetish. [Slight]

Odour threshold : 100 ppm

Important health, safety and environmental information

Boiling point : 64,5°C (148,1°F)

Melting/freezing point : -97.77°C (-144°F)

Flash point : Open cup: 15.85°C (60.5°F).

Density g/cm³ : 0.7915 g/cm³

Vapour density : 1.11 (Air = 1)

Other information

Auto-ignition temperature : 464°C (867.2°F)

10. Stability and reactivity

Stability : Stable under recommended storage and handling conditions (see section 7).

Conditions to avoid : Avoid all possible sources of ignition (spark or flame). Do not pressurise, cut, weld, braze, solder, drill, grind or expose containers to heat or sources of ignition. Do not allow vapor to accumulate in low or confined areas.

Hazardous decomposition products : These products are
carbon dioxide
carbon monoxide

11. Toxicological information

Potential acute health effects

Inhalation : Toxic by inhalation. Danger of very serious irreversible effects.

Ingestion : Toxic if swallowed. Danger of very serious irreversible effects.

Skin Contact : Toxic in contact with skin. Danger of very serious irreversible effects.

Eye contact : Adverse health effects are considered unlikely, when the product is used according to directions.

Product/ingredient name	Result	Species	Dose	Exposure	References
Methanol	LD50 Dermal	Rabbit	15800 mg/kg	-	NPIRI* 1,74,1974
	LD50 Intraperitoneal	Rat	7529 mg/kg	-	EVHPAZ 61,321,1985
	LD50 Intravenous	Rat	2131 mg/kg	-	EVHPAZ 61,321,1985
	LD50 Oral	Rat	5600 mg/kg	-	VCVGK* - ,87,1984
	TDLo Oral	Rat	3500 mg/kg	-	FAATDF 28,264,1995
	TDLo Oral	Rat	3 g/kg	-	TOXID9 72,315,2003
	TDLo Intraperitoneal	Rat	3490 mg/kg	-	VCVGK* - ,87,1984
	TDLo Oral	Rat	8 g/kg	-	TOXID9 13,14,1993

Chronic effects : No known significant effects or critical hazards.

Carcinogenicity : No known significant effects or critical hazards.

Mutagenicity : No known significant effects or critical hazards.

Teratogenicity : No known significant effects or critical hazards.

Developmental effects : No known significant effects or critical hazards.

Fertility effects : No known significant effects or critical hazards.

Inhalation : No specific data.

Ingestion : No specific data.

Skin : No specific data.

Eyes : No specific data.

Target organs : Causes damage to the following organs: gastrointestinal tract, upper respiratory tract, skin, eyes, central nervous system (CNS), eye, lens or cornea.

12. Ecological information

Environmental effects : No known significant effects or critical hazards.

Aquatic ecotoxicity

Product/ingredient name	Test	Result	Species	Exposure	References
Methanol	Acute	EC50 22200 to 23400 mg/L Fresh water	Daphnia - Water flea - Daphnia obtusa	48 hours	Environ.Toxicol.Water Qual. 11(3):255-258
	Acute	EC50 24500000 to 29350000 ug/L Fresh water	Daphnia - Water flea - Daphnia magna	48 hours	J.Water Pollut.Control Fed. 52(8):2117-2130
	Acute	EC50 13000000 to 13400000 ug/L Fresh water	Fish - Rainbow trout,donaldson trout - Oncorhynchus mykiss	96 hours	Bull.Environ.Contam.Toxicol. 37(4):615-621 (Author Communication Used)
	Acute	EC50 12700000 to 13700000 ug/L Fresh water	Fish - Bluegill - Lepomis macrochirus	96 hours	Bull.Environ.Contam.Toxicol. 37(4):615-621 (Author Communication Used)

12. Ecological information

Acute EC50 >10000000 ug/L Fresh water	Daphnia - Water flea - Daphnia magna	48 hours	Water Res. 23(4):495-499 (OECDG Data File)
Acute LC50 15400000 to 17600000 ug/L Fresh water	Fish - Bluegill - Lepomis macrochirus	96 hours	Bull.Environ.Contam.Toxicol. 37(4):615-621 (Author Communication Used)
Acute LC50 19 to 20 ml/L Fresh water	Fish - Rainbow trout,donaldson trout - Oncorhynchus mykiss	96 hours	Resour.Publ.No.160, U.S.Dep.Interior, Fish Wildl.Serv., Washington, DC :505 p. (USGS Data File)
Acute LC50 3289 to 4395 mg/L Fresh water	Daphnia - Water flea - Daphnia magna	48 hours	Ecotoxicol.Environ.Saf. 46(3):357-362
Acute LC50 10000000 to 33000000 ug/L Marine water	Fish - Hooknose - Agonus cataphractus	96 hours	Shellfish Information Leaflet No.22 (2nd Ed.), Ministry of Agric.Fish.Food, Fish.Lab.Burnham-on-Crouch, Essex, and Fish Exp.Station Conway, North Wales :12 p.
Acute LC50 20100000 to 20700000 ug/L Fresh water	Fish - Rainbow trout,donaldson trout - Oncorhynchus mykiss	96 hours	Bull.Environ.Contam.Toxicol. 37(4):615-621 (Author Communication Used)
Acute LC50 2500000 ug/L Marine water	Crustaceans - Common shrimp, sand shrimp - Crangon crangon	48 hours	Shellfish Information Leaflet No.22 (2nd Ed.), Ministry of Agric.Fish.Food, Fish.Lab.Burnham-on-Crouch, Essex, and Fish Exp.Station Conway, North Wales :12 p.
Acute LC50 >100000 ug/L Fresh water	Fish - Fathead minnow - Pimephales promelas	96 hours	Environ.Toxicol.Chem. 5(9):831-840
Acute LC50 28200000 ug/L Fresh water	Fish - Fathead minnow - Pimephales promelas	96 hours	In: W.E.Bishop, R.D.Cardwell, and B.B.Heidolph (Eds.), Aquatic Toxicology and Hazard Assessment, 6th Symposium, ASTM STP 802, Philadelphia, PA :90-97 (Most LC50 Data Publ As 12448, 12447, 12858, 12859, 3217)
Acute LC50 28000000 ug/L	Fish - Bleak -	96 hours	Chemosphere

12. Ecological information

	Marine water	Alburnus alburnus		13(5/6):613-622
	Acute LC50 >28000000 ug/L Marine water	Fish - Bleak - Alburnus alburnus	96 hours	Chemosphere 8(11/12):843-851 (Author Communication Used) (OECDG Data File)

Other adverse effects : No known significant effects or critical hazards.

13. Disposal considerations

Methods of disposal : Empty containers or liners may retain some product residues. Do not empty into drains; dispose of this material and its container in a safe way. Dispose of in accordance with all applicable local and national regulations

European waste catalogue (EWC) : 14 06 03* other solvents and solvent mixtures

Hazardous waste : This material and its container must be disposed of as hazardous waste.

Waste number : 7042

14. Transport information

International transport regulations

Regulatory information	UN number	Proper shipping name	Class	Packing group	Label	Additional information
ADR/RID Class	UN1230	METHANOL	3	II		**Hazard identification number** 336 **Limited quantity** LQ0 **CEFIC Tremcard** 30S1230
IMDG Class	UN1230	METHANOL	3	II		**Emergency schedules (EmS)** F-E, S-D
IATA-DGR Class	UN1230	METHANOL	3	II		**Passenger and Cargo Aircraft** Quantity limitation: 1 L **Cargo Aircraft Only** Quantity limitation: 60 L **Limited Quantities - Passenger Aircraft** Quantity limitation: 1 L

15. Regulatory information

EU regulations

Product use : Industrial applications.

Classification and labelling have been performed according to EU Directives 67/548/EEC and 1999/45/EC (including amendments) and the intended use.

Europe inventory : **Europe inventory:** This material is listed or exempted.

Other EU regulations

Child protection : Yes, applicable.

Tactile warning of danger : Yes, applicable.

National regulations

Hazard symbol or symbols :

Highly flammable, Toxic

Risk phrases : ◤R11- Highly flammable.
R23/24/25- Toxic by inhalation, in contact with skin and if swallowed.
R39/23/24/25- Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.

Safety phrases : S1/2- Keep locked up and out of the reach of children.
S7- Keep container tightly closed.
S16- Keep away from sources of ignition - No smoking.
S36/37- Wear suitable protective clothing and gloves.
S45- In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

Carcinogenic class : Not classified.

Contains EINECS number : ◤Methanol 200-659-6

16. Other information

Full text of R-phrases referred to in sections 2 and 3 - Norway : ◤R11- Highly flammable.
R23/24/25- Toxic by inhalation, in contact with skin and if swallowed.
R39/23/24/25- Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.

Full text of classifications referred to in sections 2 and 3 - Norway : ◤F - Highly flammable
T - Toxic

References : European Chemical Bureau, Annex 1 EU Directive 67/548/EEC
National Institute for Occupational Safety and Health, U.S. Dept. of Health, Education, and Welfare, Reports and Memoranda
Registry of Toxic Effects of Chemical Substances
Atrion International Inc. 4777 Levy Street, St Laurent, Quebec HAR 2P9, Canada

History

Date of printing : **2008-01-16.**

Date of issue/Date of revision : **2008-01-16.**

Date of previous issue : **2006-03-23.**

Version : **3**

Prepared by : Yara Product Classification and Regulations

◤ **Indicates information that has changed from previously issued version.**

Notice to reader

To the best of our knowledge, the information provided in this Safety Data Sheet is accurate as at the date of its issue. The information it contains is being given for safety guidance purposes and relates only to the specific material and uses described in it. This information does not necessarily apply to that material when combined with other material(s) or when used otherwise than as described herein. Final determination of the suitability of any material is the sole responsibility of the user. All materials may represent unknown hazards and should be used with caution. Yara International ASA disclaims any liability for loss or damage resulting from the use of any data, information or recommendations set out in this Safety Data Sheet.

SIGMA-ALDRICH

sigma-aldrich.com

Material Safety Data Sheet

Version 3.1
Revision Date 03/01/2010
Print Date 12/09/2010

1. PRODUCT AND COMPANY IDENTIFICATION

Product name : Copper(II) nitrate hemi(pentahydrate)

Product Number : 31288
Brand : Sigma-Aldrich

Company : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USA
Telephone : +18003255832
Fax : +18003255052
Emergency Phone # : (314) 776-6555

2. HAZARDS IDENTIFICATION

Emergency Overview

OSHA Hazards

Oxidizer, Target Organ Effect, Harmful by ingestion., Irritant

Target Organs

Blood, Kidney, Liver, Central nervous system, Vascular system.

GHS Label elements, including precautionary statements

Pictogram

Signal word Danger

Hazard statement(s)

H272	May intensify fire; oxidiser.
H302	Harmful if swallowed.
H315	Causes skin irritation.
H318	Causes serious eye damage.
H400	Very toxic to aquatic life.

Precautionary statement(s)

P210	Keep away from heat.
P220	Keep/Store away from clothing/ combustible materials.
P221	Take any precaution to avoid mixing with combustibles.
P264	Wash skin thoroughly after handling.
P270	Do not eat, drink or smoke when using this product.
P273	Avoid release to the environment.
P280	Wear protective gloves/protective clothing/eye protection/face protection.
P301 + P312	IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell.
P302 + P352	IF ON SKIN: Wash with plenty of soap and water.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P310	Immediately call a POISON CENTER or doctor/physician.
P321	Specific treatment (see supplemental first aid instructions on this label).
P330	Rinse mouth.
P332 + P313	If skin irritation occurs: Get medical advice/attention.
P362	Take off contaminated clothing and wash before reuse.
P370 + P378	In case of fire: Use dry sand, dry chemical or alcohol-resistant foam for extinction.

P391	Collect spillage.
P501	Dispose of contents/container to an approved waste disposal plant.

HMIS Classification

Health hazard:	2
Chronic Health Hazard:	*
Flammability:	0
Physical hazards:	2

NFPA Rating

Health hazard:	2
Fire:	0
Reactivity Hazard:	2
Special hazard.:	OX

Potential Health Effects

Inhalation	May be harmful if inhaled. Causes respiratory tract irritation.
Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes eye irritation.
Ingestion	Harmful if swallowed.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms : Cupric nitratehemi(pentahydrate)

Formula : $CuN_2O_6 \cdot 2.5H_2O$

Molecular Weight : 232.59 g/mol

CAS-No.	EC-No.	Index-No.	Concentration
Copper(II) nitrate hydrate			
19004-19-4	221-838-5	-	-

4. FIRST AID MEASURES

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.Move out of dangerous area.

If inhaled
If breathed in, move person into fresh air. If not breathing give artificial respiration Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

Further information
Use water spray to cool unopened containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Use personal protective equipment. Avoid dust formation. Avoid breathing dust. Ensure adequate ventilation. Evacuate personnel to safe areas.

Environmental precautions
Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

Methods and materials for containment and cleaning up
Pick up and arrange disposal without creating dust. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Precautions for safe handling
Avoid contact with skin and eyes. Avoid formation of dust and aerosols.
Provide appropriate exhaust ventilation at places where dust is formed. Keep away from sources of ignition - No smoking. Keep away from combustible material.

Conditions for safe storage
Keep container tightly closed in a dry and well-ventilated place.

Heat sensitive. Moisture sensitive.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Contains no substances with occupational exposure limit values.

Personal protective equipment

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
Handle with gloves.

Eye protection
Safety glasses with side-shields conforming to EN166

Skin and body protection
Choose body protection according to the amount and concentration of the dangerous substance at the work place.

Hygiene measures
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	solid

Safety data

pH	no data available
Melting point	114 °C (237 °F)
Boiling point	no data available
Flash point	not applicable
Ignition temperature	no data available
Lower explosion limit	no data available
Upper explosion limit	no data available
Density	2.320 g/cm3
Water solubility	no data available

10. STABILITY AND REACTIVITY

Chemical stability
Stable under recommended storage conditions.

Conditions to avoid
Heat. Avoid moisture.

Materials to avoid
Reducing agents, Organic materials, Powdered metals

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - nitrogen oxides (NOx), Copper oxides

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11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 Oral - rat - 794 mg/kg
Remarks: Behavioral:Somnolence (general depressed activity). Behavioral:Convulsions or effect on seizure threshold.

Skin corrosion/irritation
Skin - rabbit - Skin irritation

Serious eye damage/eye irritation
Eyes - rabbit - Severe eye irritation

Respiratory or skin sensitization
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
ACGIH:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure (GHS)
no data available

Specific target organ toxicity - repeated exposure (GHS)
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. Causes respiratory tract irritation.
Ingestion	Harmful if swallowed.
Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes eye irritation.

Signs and Symptoms of Exposure

Symptoms of systemic copper poisoning may include: capillary damage, headache, cold sweat, weak pulse, and kidney and liver damage, central nervous system excitation followed by depression, jaundice, convulsions, paralysis, and coma. Death may occur from shock or renal failure. Chronic copper poisoning is typified by hepatic cirrhosis, brain damage and demyelination, kidney defects, and copper deposition in the cornea as exemplified by humans with Wilson's disease. It has also been reported that copper poisoning has lead to hemolytic anemia and accelerates arteriosclerosis., Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin., Cough, Shortness of breath, Headache

Additional Information
RTECS: QU7400000

12. ECOLOGICAL INFORMATION

Toxicity

Toxicity to fish	LC50 - other fish - 0.29 mg/l - 96.0 h

Persistence and degradability
The methods for determining the biological degradability are not applicable to inorganic substances.

Bioaccumulative potential
no data available

Mobility in soil
no data available

PBT and vPvB assessment
no data available

Other adverse effects

An environmental hazard cannot be excluded in the event of unprofessional handling or disposal.

Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

13. DISPOSAL CONSIDERATIONS

Product
Observe all federal, state, and local environmental regulations. Contact a licensed professional waste disposal service to dispose of this material.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
UN-Number: 3085 Class: 5.1 (8) Packing group: II
Proper shipping name: Oxidizing solid, corrosive, n.o.s. (Copper(II) nitrate hydrate)
Reportable Quantity (RQ): 100 lbs
Marine pollutant: No
Poison Inhalation Hazard: No

IMDG
UN-Number: 3085 Class: 5.1 (8) Packing group: II EMS-No: F-A, S-Q
Proper shipping name: OXIDIZING SOLID, CORROSIVE, N.O.S. (Copper(II) nitrate hydrate)
Marine pollutant: No

IATA
UN-Number: 3085 Class: 5.1 (8) Packing group: II
Proper shipping name: Oxidizing solid, corrosive, n.o.s. (Copper(II) nitrate hydrate)

15. REGULATORY INFORMATION

OSHA Hazards
Oxidizer, Target Organ Effect, Harmful by ingestion., Irritant

DSL Status
All components of this product are on the Canadian DSL list.

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components

	CAS-No.	Revision Date
Copper(II) nitrate hydrate	19004-19-4	1993-04-24

SARA 311/312 Hazards
Reactivity Hazard, Acute Health Hazard, Chronic Health Hazard

Massachusetts Right To Know Components

	CAS-No.	Revision Date
Copper(II) nitrate hydrate	19004-19-4	1993-04-24

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Copper(II) nitrate hydrate	19004-19-4	1993-04-24

New Jersey Right To Know Components

	CAS-No.	Revision Date
Copper(II) nitrate hydrate	19004-19-4	1993-04-24

California Prop. 65 Components
This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

16. OTHER INFORMATION

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Co., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale.

SIGMA-ALDRICH

Material Safety Data Sheet

Version 3.0
Revision Date 12/28/2008
Print Date 12/09/2010

1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	Zinc nitrate hexahydrate
Product Number	:	96482
Brand	:	Sigma-Aldrich
Company	:	Sigma-Aldrich 3050 Spruce Street SAINT LOUIS MO 63103 USA
Telephone	:	+18003255832
Fax	:	+18003255052
Emergency Phone #	:	(314) 776-6555

2. COMPOSITION/INFORMATION ON INGREDIENTS

Formula	:	$N_2O_6Zn \cdot 6H_2O$
Molecular Weight	:	297.49 g/mol

CAS-No.	EC-No.	Index-No.	Concentration
Zinc nitrate hexahydrate			
10196-18-6	231-943-8	-	-

3. HAZARDS IDENTIFICATION

Emergency Overview

OSHA Hazards
Oxidizer, Target Organ Effect, Harmful by ingestion., Corrosive

Target Organs

Blood, Central nervous system

HMIS Classification

Health Hazard:	3
Chronic Health Hazard:	*
Flammability:	0
Physical hazards:	2

NFPA Rating

Health Hazard:	3
Fire:	0
Reactivity Hazard:	2
Special hazard.:	OX

Potential Health Effects

Inhalation May be harmful if inhaled. Material is extremely destructive to the tissue of the

	mucous membranes and upper respiratory tract.
Skin	May be harmful if absorbed through skin. Causes skin burns.
Eyes	Causes eye burns.
Ingestion	Harmful if swallowed. Causes burns.

4. FIRST AID MEASURES

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.Move out of dangerous area.

If inhaled
If breathed in, move person into fresh air. If not breathing give artificial respiration Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Continue rinsing eyes during transport to hospital.Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIRE-FIGHTING MEASURES

Flammable properties

Flash point	not applicable
Ignition temperature	no data available

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

Further information
Use water spray to cool unopened containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Use personal protective equipment. Avoid dust formation. Avoid breathing dust. Ensure adequate ventilation. Evacuate personnel to safe areas.

Environmental precautions
Do not let product enter drains.

Methods for cleaning up
Pick up and arrange disposal without creating dust. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Handling
Avoid contact with skin and eyes. Avoid formation of dust and aerosols.
Provide appropriate exhaust ventilation at places where dust is formed. Keep away from sources of ignition - No smoking. Keep away from combustible material.

Storage
Keep container tightly closed in a dry and well-ventilated place.

hygroscopic

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Contains no substances with occupational exposure limit values.

Personal protective equipment

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Where risk assessment shows air-purifying respirators are appropriate use a dust mask type N95 (US) or type P1 (EN 143) respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
Handle with gloves.

Eye protection
Safety glasses

Skin and body protection
Choose body protection according to the amount and concentration of the dangerous substance at the work place.

Hygiene measures
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	crystalline
Colour	colourless

Safety data

pH	no data available
Melting point	36 °C (97 °F)
Boiling point	no data available
Flash point	not applicable
Ignition temperature	no data available
Lower explosion limit	no data available
Upper explosion limit	no data available
Density	2.065 g/cm3
Water solubility	no data available

10. STABILITY AND REACTIVITY

Storage stability
Stable under recommended storage conditions.

Conditions to avoid
hygroscopic

Materials to avoid
Powdered metals, Cyanides, Sodium hypophosphite, Stannous chloride, Thiocyanates, Strong reducing agents

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Zinc/zinc oxides

11. TOXICOLOGICAL INFORMATION

Acute toxicity

LD50 Oral - rat - 1,190 mg/kg

Irritation and corrosion

Skin - rabbit - Severe skin irritation - 24 h

Eyes - rabbit - Moderate eye irritation - 24 h

Sensitisation

no data available

Chronic exposure

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
ACGIH:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Signs and Symptoms of Exposure

Fever, Cough, Nausea, Vomiting, Weakness

Potential Health Effects

Inhalation	May be harmful if inhaled. Material is extremely destructive to the tissue of the mucous membranes and upper respiratory tract.
Skin	May be harmful if absorbed through skin. Causes skin burns.
Eyes	Causes eye burns.
Ingestion	Harmful if swallowed. Causes burns.
Target Organs	Blood, Central nervous system,

Additional Information
RTECS: ZH4775000

12. ECOLOGICAL INFORMATION

Elimination information (persistence and degradability)

no data available

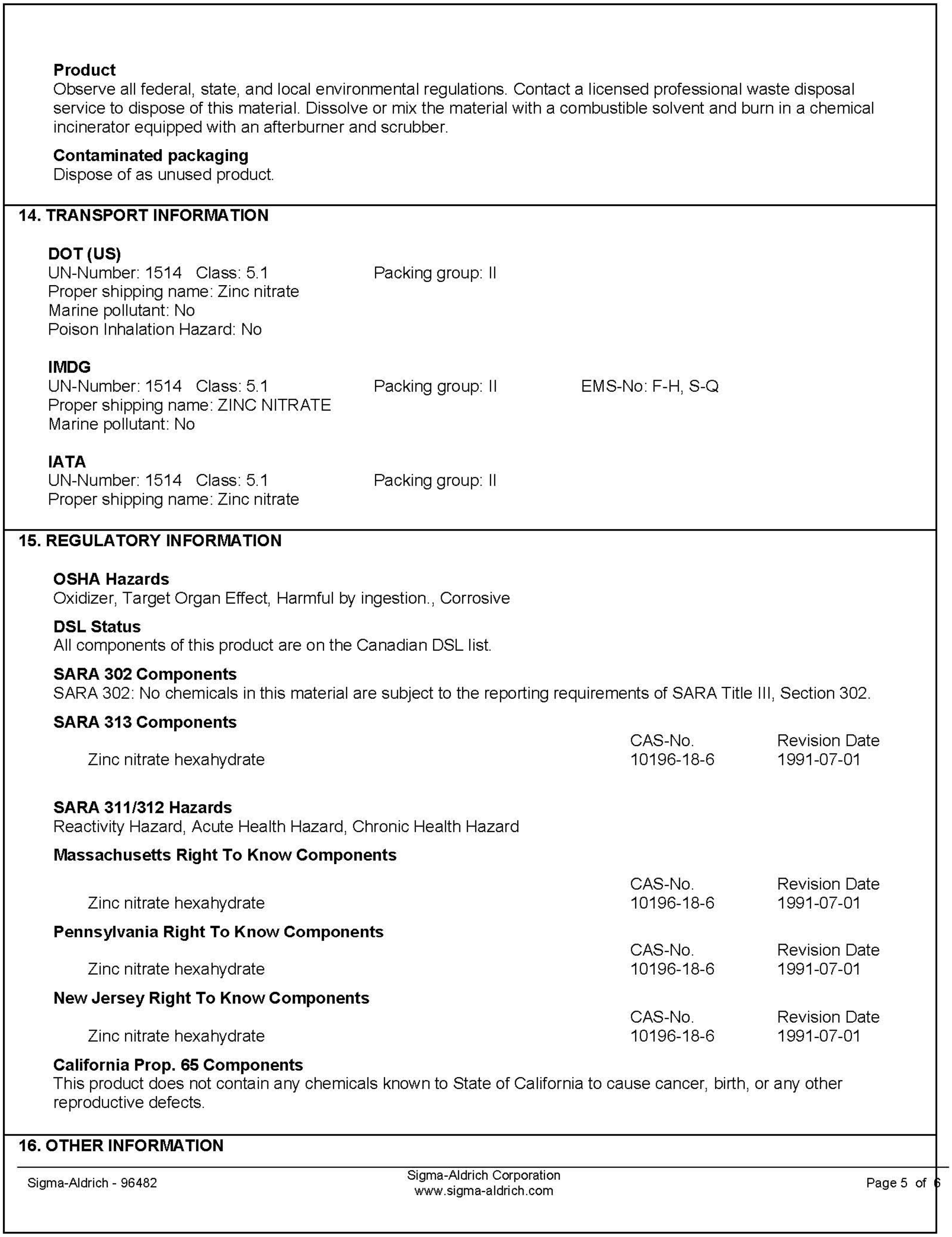
Ecotoxicity effects

no data available

Further information on ecology

no data available

13. DISPOSAL CONSIDERATIONS



Product
Observe all federal, state, and local environmental regulations. Contact a licensed professional waste disposal service to dispose of this material. Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
UN-Number: 1514 Class: 5.1 Packing group: II
Proper shipping name: Zinc nitrate
Marine pollutant: No
Poison Inhalation Hazard: No

IMDG
UN-Number: 1514 Class: 5.1 Packing group: II EMS-No: F-H, S-Q
Proper shipping name: ZINC NITRATE
Marine pollutant: No

IATA
UN-Number: 1514 Class: 5.1 Packing group: II
Proper shipping name: Zinc nitrate

15. REGULATORY INFORMATION

OSHA Hazards
Oxidizer, Target Organ Effect, Harmful by ingestion., Corrosive

DSL Status
All components of this product are on the Canadian DSL list.

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components

	CAS-No.	Revision Date
Zinc nitrate hexahydrate	10196-18-6	1991-07-01

SARA 311/312 Hazards
Reactivity Hazard, Acute Health Hazard, Chronic Health Hazard

Massachusetts Right To Know Components

	CAS-No.	Revision Date
Zinc nitrate hexahydrate	10196-18-6	1991-07-01

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Zinc nitrate hexahydrate	10196-18-6	1991-07-01

New Jersey Right To Know Components

	CAS-No.	Revision Date
Zinc nitrate hexahydrate	10196-18-6	1991-07-01

California Prop. 65 Components
This product does not contain any chemicals known to State of California to cause cancer, birth, or any other reproductive defects.

16. OTHER INFORMATION

Further information

SIGMA-ALDRICH

Material Safety Data Sheet

Version 3.0
Revision Date 01/02/2009
Print Date 12/09/2010

1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	Aluminum nitrate nonahydrate
Product Number	:	237973
Brand	:	Sigma-Aldrich
Company	:	Sigma-Aldrich 3050 Spruce Street SAINT LOUIS MO 63103 USA
Telephone	:	+18003255832
Fax	:	+18003255052
Emergency Phone #	:	(314) 776-6555

2. COMPOSITION/INFORMATION ON INGREDIENTS

Formula	:	$AlN_3O_9 \cdot 9H_2O$
Molecular Weight	:	375.13 g/mol

CAS-No.	EC-No.	Index-No.	Concentration
Aluminium nitrate			
7784-27-2	236-751-8	-	-

3. HAZARDS IDENTIFICATION

Emergency Overview

OSHA Hazards
Oxidizer, Irritant

HMIS Classification

Health Hazard:	2
Flammability:	0
Physical hazards:	1

NFPA Rating

Health Hazard:	2
Fire:	0
Reactivity Hazard:	1
Special hazard.:	OX

Potential Health Effects

Inhalation	May be harmful if inhaled. Causes respiratory tract irritation.
Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes eye irritation.
Ingestion	May be harmful if swallowed.

4. FIRST AID MEASURES

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.Move out of dangerous area.

If inhaled
If breathed in, move person into fresh air. If not breathing give artificial respiration Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIRE-FIGHTING MEASURES

Flammable properties

Flash point	not applicable
Ignition temperature	no data available

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

Further information
Use water spray to cool unopened containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Use personal protective equipment. Avoid dust formation. Avoid breathing dust. Ensure adequate ventilation. Evacuate personnel to safe areas.

Environmental precautions
Do not let product enter drains.

Methods for cleaning up
Pick up and arrange disposal without creating dust. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Handling
Avoid contact with skin and eyes. Avoid formation of dust and aerosols.
Provide appropriate exhaust ventilation at places where dust is formed. Keep away from sources of ignition - No smoking. Keep away from combustible material.

Storage
Keep container tightly closed in a dry and well-ventilated place.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Components with workplace control parameters

Components	CAS-No.	Value	Control parameters	Update	Basis
Aluminium nitrate	7784-27-2	TWA	2 mg/m3	1989-03-01	US. Department of Labor -

					Occupational Safety and Health Administration (OSHA) 29 CFR 1910.1000 Z-1-A
		TWA	2 mg/m3	1994-09-01	US. American Conference of Governmental and Industrial Hygienists Threshold Limit Values for Chemical Substances in the Work Environment; Annual Reports for the Year 2004:Committees on Threshold Limit Values (TLVs) and Biological Exposure Indices (BEIs)

Personal protective equipment

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Where risk assessment shows air-purifying respirators are appropriate use a dust mask type N95 (US) or type P1 (EN 143) respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
Handle with gloves.

Eye protection
Safety glasses

Skin and body protection
Choose body protection according to the amount and concentration of the dangerous substance at the work place.

Hygiene measures
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	solid
Colour	colourless

Safety data

pH	2.5 - 3.5 at 50 g/l at 25 °C (77 °F)
Melting point	73 °C (163 °F)
Boiling point	no data available
Flash point	not applicable
Ignition temperature	no data available
Lower explosion limit	no data available
Upper explosion limit	no data available
Water solubility	no data available

10. STABILITY AND REACTIVITY

Storage stability
Stable under recommended storage conditions.

Conditions to avoid
Avoid moisture.

Materials to avoid
Strong reducing agents, Powdered metals, Strong acids

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - nitrogen oxides (NOx), Aluminum oxide

11. TOXICOLOGICAL INFORMATION

Acute toxicity

LD50 Oral - rat - 3,671 mg/kg
Remarks: Behavioral:Somnolence (general depressed activity). Gastrointestinal:Changes in structure or function of salivary glands.

Irritation and corrosion

no data available

Sensitisation

no data available

Chronic exposure

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
ACGIH:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Developmental Toxicity - rat - Oral
Effects on Embryo or Fetus: Fetotoxicity (except death, e.g., stunted fetus). Effects on Embryo or Fetus: Fetal death. Specific Developmental Abnormalities: Craniofacial (including nose and tongue).

Developmental Toxicity - rat - Oral
Specific Developmental Abnormalities: Musculoskeletal system.

Developmental Toxicity - rat - Oral
Specific Developmental Abnormalities: Cardiovascular (circulatory) system.

Reproductive toxicity - rat - Oral
Effects on Newborn: Physical.

Signs and Symptoms of Exposure

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Potential Health Effects

Inhalation	May be harmful if inhaled. Causes respiratory tract irritation.
Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes eye irritation.
Ingestion	May be harmful if swallowed.

Additional Information
RTECS: BD1050000

12. ECOLOGICAL INFORMATION

Elimination information (persistence and degradability)

no data available

Ecotoxicity effects

no data available

Further information on ecology

no data available

13. DISPOSAL CONSIDERATIONS

Product
Observe all federal, state, and local environmental regulations. Contact a licensed professional waste disposal service to dispose of this material.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
UN-Number: 1438 Class: 5.1 Packing group: III
Proper shipping name: Aluminum nitrate
Marine pollutant: No
Poison Inhalation Hazard: No

IMDG
UN-Number: 1438 Class: 5.1 Packing group: III EMS-No: F-A, S-Q
Proper shipping name: ALUMINIUM NITRATE
Marine pollutant: No

IATA
UN-Number: 1438 Class: 5.1 Packing group: III
Proper shipping name: Aluminium nitrate

15. REGULATORY INFORMATION

OSHA Hazards
Oxidizer, Irritant

DSL Status
All components of this product are on the Canadian DSL list.

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards
Reactivity Hazard, Acute Health Hazard

Massachusetts Right To Know Components
No components are subject to the Massachusetts Right to Know Act.

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Aluminium nitrate	7784-27-2	1989-12-01

New Jersey Right To Know Components

	CAS-No.	Revision Date
Aluminium nitrate	7784-27-2	1989-12-01

California Prop. 65 Components
This product does not contain any chemicals known to State of California to cause cancer, birth, or any other reproductive defects.

16. OTHER INFORMATION

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Co., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale.

SIGMA-ALDRICH sigma-aldrich.com

Material Safety Data Sheet

Version 4.0
Revision Date 07/19/2010
Print Date 12/09/2010

1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	Sodium carbonate
Product Number	:	204420
Brand	:	Aldrich
Company	:	Sigma-Aldrich 3050 Spruce Street SAINT LOUIS MO 63103 USA
Telephone	:	+18003255832
Fax	:	+18003255052
Emergency Phone #	:	(314) 776-6555

2. HAZARDS IDENTIFICATION

Emergency Overview

OSHA Hazards
Irritant

GHS Label elements, including precautionary statements

Pictogram	
Signal word	Danger

Hazard statement(s)

H303	May be harmful if swallowed.
H314	Causes severe skin burns and eye damage.

Precautionary statement(s)

P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P310	Immediately call a POISON CENTER or doctor/physician.

HMIS Classification

Health hazard:	2
Flammability:	0
Physical hazards:	0

NFPA Rating

Health hazard:	2
Fire:	0
Reactivity Hazard:	0

Potential Health Effects

Inhalation	May be harmful if inhaled. Causes respiratory tract irritation.
Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes eye irritation.
Ingestion	May be harmful if swallowed.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms	:	Soda ash

Formula : CNa_2O_3
Molecular Weight : 105.99 g/mol

CAS-No.	EC-No.	Index-No.	Concentration
Sodium carbonate			
497-19-8	207-838-8	011-005-00-2	-

4. FIRST AID MEASURES

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance. Move out of dangerous area.

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact
Take off contaminated clothing and shoes immediately. Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician. Continue rinsing eyes during transport to hospital.

If swallowed
Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media
Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

Further information
The product itself does not burn.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Use personal protective equipment. Avoid dust formation. Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Evacuate personnel to safe areas. Avoid breathing dust.

Environmental precautions
Do not let product enter drains.

Methods and materials for containment and cleaning up
Pick up and arrange disposal without creating dust. Sweep up and shovel. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Precautions for safe handling
Avoid formation of dust and aerosols.
Provide appropriate exhaust ventilation at places where dust is formed.

Conditions for safe storage
Keep container tightly closed in a dry and well-ventilated place.

hygroscopic Keep in a dry place.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Contains no substances with occupational exposure limit values.

Personal protective equipment

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face particle respirator type N100 (US) or type P3 (EN 143) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Eye protection
Face shield and safety glasses Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin and body protection
Complete suit protecting against chemicals, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Hygiene measures
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	powder
Colour	white

Safety data

pH	12 at 106 g/l at 25 °C (77 °F)
Melting point	851 °C (1,564 °F)
Boiling point	no data available
Flash point	no data available
Ignition temperature	no data available
Lower explosion limit	no data available
Upper explosion limit	no data available
Density	2.532 g/cm3
Water solubility	106 g/l at 20 °C (68 °F) - completely soluble

10. STABILITY AND REACTIVITY

Chemical stability
hygroscopic Stable under recommended storage conditions.

Conditions to avoid
Exposure to moisture.

Materials to avoid
Strong acids

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Carbon oxides

11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 Oral - rat - 4,090 mg/kg

LC50 Inhalation - rat - 2 h - 5,750 mg/l

Skin corrosion/irritation
Skin - rabbit - Mild skin irritation - 24 h

Serious eye damage/eye irritation
Eyes - rabbit - Eye irritation - 24 h

Respiratory or skin sensitization
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
ACGIH:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure (GHS)
no data available

Specific target organ toxicity - repeated exposure (GHS)
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. Causes respiratory tract irritation.
Ingestion	May be harmful if swallowed.
Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes eye irritation.

Signs and Symptoms of Exposure
burning sensation, Cough, wheezing, laryngitis, Shortness of breath, Headache, Nausea, Vomiting

Additional Information
RTECS: VZ4050000

12. ECOLOGICAL INFORMATION

Toxicity

Toxicity to fish	LC50 - Lepomis macrochirus (Bluegill) - 300 mg/l - 96 h
Toxicity to daphnia and other aquatic invertebrates.	EC50 - Daphnia magna (Water flea) - 265 mg/l - 48 h

Persistence and degradability
no data available

Bioaccumulative potential
no data available

Mobility in soil
no data available

PBT and vPvB assessment
no data available

Other adverse effects

no data available

13. DISPOSAL CONSIDERATIONS

Product
Offer surplus and non-recyclable solutions to a licensed disposal company. Contact a licensed professional waste disposal service to dispose of this material.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
Not dangerous goods

IMDG
Not dangerous goods

IATA
Not dangerous goods

15. REGULATORY INFORMATION

OSHA Hazards
Irritant

DSL Status
All components of this product are on the Canadian DSL list.

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards
Acute Health Hazard

Massachusetts Right To Know Components
No components are subject to the Massachusetts Right to Know Act.

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Sodium carbonate	497-19-8	

New Jersey Right To Know Components

	CAS-No.	Revision Date
Sodium carbonate	497-19-8	

California Prop. 65 Components
This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

16. OTHER INFORMATION

Further information

SIGMA-ALDRICH

sigma-aldrich.com

Material Safety Data Sheet

Version 4.0
Revision Date 02/26/2010
Print Date 12/09/2010

1. PRODUCT AND COMPANY IDENTIFICATION

Product name : Sodium acetate

Product Number : 32319
Brand : Sigma-Aldrich

Company : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USA
Telephone : +18003255832
Fax : +18003255052
Emergency Phone # : (314) 776-6555

2. HAZARDS IDENTIFICATION

Emergency Overview

OSHA Hazards
No known OSHA hazards

GHS Label elements, including precautionary statements

Pictogram	none
Signal word	Warning

Hazard statement(s)

H303 + H333	May be harmful if swallowed or if inhaled.
H316	Causes mild skin irritation.
H320	Causes eye irritation.

Precautionary statement(s)

P264	Wash skin thoroughly after handling.
P304 + P312	IF INHALED: Call a POISON CENTER or doctor/physician if you feel unwell.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P312	Call a POISON CENTER or doctor/physician if you feel unwell.
P332 + P313	If skin irritation occurs: Get medical advice/attention.
P337 + P313	If eye irritation persists: Get medical advice/attention.

HMIS Classification
Health hazard: 1
Flammability: 0
Physical hazards: 1

NFPA Rating
Health hazard: 1
Fire: 0
Reactivity Hazard: 1

Potential Health Effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.
Ingestion	May be harmful if swallowed.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms : Acetic acidsodium salt

Formula : $C_2H_3NaO_2$
Molecular Weight : 82.03 g/mol

CAS-No.	EC-No.	Index-No.	Concentration
Sodium acetate			
127-09-3	204-823-8	-	-

4. FIRST AID MEASURES

If inhaled
If breathed in, move person into fresh air. If not breathing give artificial respiration

In case of skin contact
Wash off with soap and plenty of water.

In case of eye contact
Flush eyes with water as a precaution.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Avoid dust formation.

Environmental precautions
Do not let product enter drains.

Methods and materials for containment and cleaning up
Sweep up and shovel. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Precautions for safe handling
Provide appropriate exhaust ventilation at places where dust is formed. Normal measures for preventive fire protection.

Conditions for safe storage
Keep container tightly closed in a dry and well-ventilated place.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Contains no substances with occupational exposure limit values.

Personal protective equipment

Respiratory protection
Respiratory protection is not required. Where protection from nuisance levels of dusts are desired, use type N95 (US) or type P1 (EN 143) dust masks. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
For prolonged or repeated contact use protective gloves.

Eye protection
Safety glasses

Hygiene measures
General industrial hygiene practice.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	solid
Colour	white

Safety data

pH	8.5 - 9.9 at 246 g/l at 25 °C (77 °F)
Melting point	> 300 °C (> 572 °F)
Boiling point	no data available
Flash point	> 250 °C (> 482 °F) - closed cup
Ignition temperature	600 °C (1,112 °F)
Lower explosion limit	no data available
Upper explosion limit	no data available
Density	1.528 g/cm3
Water solubility	246 g/l at 20 °C (68 °F) - completely soluble
Partition coefficient: n-octanol/water	log Pow: -4.22

10. STABILITY AND REACTIVITY

Chemical stability
Stable under recommended storage conditions.

Conditions to avoid
Exposure to moisture.

Materials to avoid
Strong oxidizing agents

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Carbon oxides, Sodium/sodium oxides

11. TOXICOLOGICAL INFORMATION

Acute toxicity
LD50 Oral - rat - 3,530 mg/kg

LC50 Inhalation - rat - 1 h - > 30,000 mg/m3

LD50 Dermal - rabbit - > 10,000 mg/kg

Skin corrosion/irritation
Skin - rabbit - Mild skin irritation - 24 h

Serious eye damage/eye irritation
Eyes - rabbit - Mild eye irritation

Respiratory or skin sensitization
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
ACGIH:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure (GHS)
no data available

Specific target organ toxicity - repeated exposure (GHS)
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Ingestion	May be harmful if swallowed.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.

Signs and Symptoms of Exposure
Abdominal pain, Nausea, Vomiting

Additional Information
RTECS: AJ4300010

12. ECOLOGICAL INFORMATION

Toxicity

Toxicity to fish	LC50 - Pimephales promelas (fathead minnow) - 13,330 mg/l - 120 h
	LC50 - Lepomis macrochirus (Bluegill) - 5,000 mg/l - 24 h
Toxicity to daphnia and other aquatic invertebrates.	EC50 - Daphnia magna (Water flea) - > 1,000 mg/l - 48 h

Persistence and degradability

Biodegradability	Result: 99 % - Readily biodegradable.

Bioaccumulative potential
no data available

Mobility in soil
no data available

PBT and vPvB assessment
no data available

Other adverse effects

no data available

13. DISPOSAL CONSIDERATIONS

Product
Observe all federal, state, and local environmental regulations.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
Not dangerous goods

IMDG
Not dangerous goods

IATA
Not dangerous goods

15. REGULATORY INFORMATION

OSHA Hazards
No known OSHA hazards

DSL Status
All components of this product are on the Canadian DSL list.

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards
No SARA Hazards

Massachusetts Right To Know Components
No Components Listed

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Sodium acetate	127-09-3	

New Jersey Right To Know Components

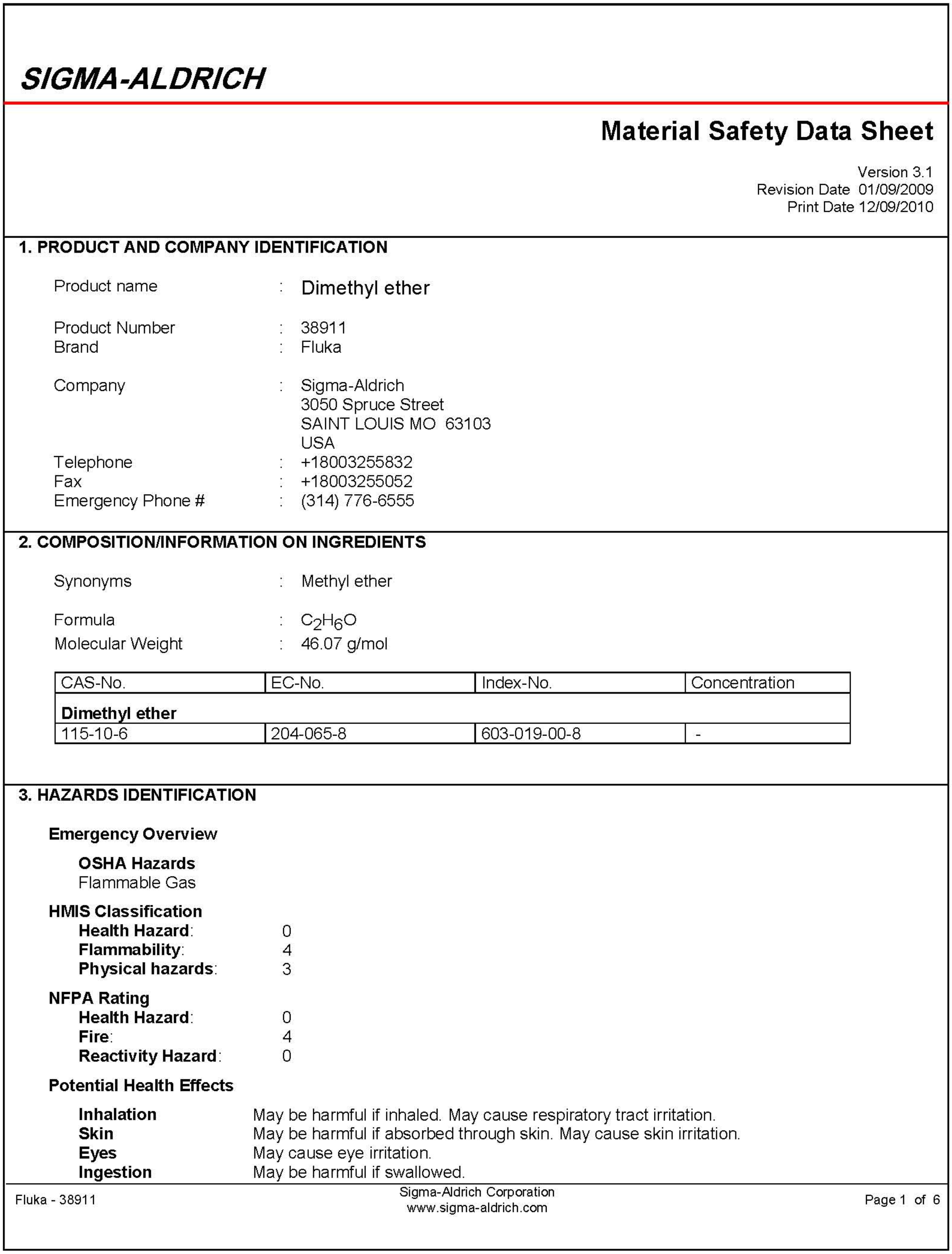
	CAS-No.	Revision Date
Sodium acetate	127-09-3	

California Prop. 65 Components
This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

16. OTHER INFORMATION

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Co., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale.



SIGMA-ALDRICH

Material Safety Data Sheet

Version 3.1
Revision Date 01/09/2009
Print Date 12/09/2010

1. PRODUCT AND COMPANY IDENTIFICATION

Product name : Dimethyl ether

Product Number : 38911
Brand : Fluka

Company : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USA
Telephone : +18003255832
Fax : +18003255052
Emergency Phone # : (314) 776-6555

2. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms : Methyl ether

Formula : C_2H_6O
Molecular Weight : 46.07 g/mol

CAS-No.	EC-No.	Index-No.	Concentration
Dimethyl ether			
115-10-6	204-065-8	603-019-00-8	-

3. HAZARDS IDENTIFICATION

Emergency Overview

OSHA Hazards
Flammable Gas

HMIS Classification

Health Hazard:	0
Flammability:	4
Physical hazards:	3

NFPA Rating

Health Hazard:	0
Fire:	4
Reactivity Hazard:	0

Potential Health Effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.
Ingestion	May be harmful if swallowed.

4. FIRST AID MEASURES

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance. Move out of dangerous area.

If inhaled
If breathed in, move person into fresh air. If not breathing give artificial respiration Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Flush eyes with water as a precaution.

If swallowed
Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIRE-FIGHTING MEASURES

Flammable properties

Flash point	-41 °C (-42 °F) - closed cup
Ignition temperature	240 °C (464 °F)

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

Further information
Use water spray to cool unopened containers.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.

Environmental precautions
Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

Methods for cleaning up
Wipe up with absorbent material (e.g. cloth, fleece).

7. HANDLING AND STORAGE

Handling
Avoid inhalation of vapour or mist.
Use explosion-proof equipment. Keep away from sources of ignition - No smoking. Take measures to prevent the build up of electrostatic charge.

Storage
Keep container tightly closed in a dry and well-ventilated place. Store in cool place.

Contents under pressure.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Contains no substances with occupational exposure limit values.

Personal protective equipment

Respiratory protection
Respiratory protection is not required. Where protection is desired, use multi-purpose combination (US) or type AXBEK (EN 14387) respirator cartridges. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
For prolonged or repeated contact use protective gloves.

Eye protection
Safety glasses

Skin and body protection
Choose body protection according to the amount and concentration of the dangerous substance at the work place.

Hygiene measures
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	gaseous

Safety data

pH	no data available
Melting point	-141 °C (-222 °F)
Boiling point	24.8 °C (76.6 °F)
Flash point	-41 °C (-42 °F) - closed cup
Ignition temperature	240 °C (464 °F)
Lower explosion limit	3.4 %(V)
Upper explosion limit	27 %(V)
Vapour pressure	5,333 hPa (4,000 mmHg) at 20 °C (68 °F)
Water solubility	no data available
Relative vapour density	1.59 - (Air = 1.0)

10. STABILITY AND REACTIVITY

Storage stability
Stable under recommended storage conditions.

Conditions to avoid
Heat, flames and sparks.

Materials to avoid
Strong oxidizing agents, Strong acids

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Carbon oxides

11. TOXICOLOGICAL INFORMATION

Acute toxicity

LC50 Inhalation - rat - 308,000 mg/m3
Remarks: Behavioral:General anesthetic.

Irritation and corrosion

no data available

Sensitisation

no data available

Chronic exposure

IARC:	No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.
ACGIH:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.
NTP:	No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA:	No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Signs and Symptoms of Exposure

Blurred vision, Headache, Dizziness, Convulsions, Asphyxia, Unconsciousness, Liver disorders

Potential Health Effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.
Ingestion	May be harmful if swallowed.

Additional Information
RTECS: PM4780000

12. ECOLOGICAL INFORMATION

Elimination information (persistence and degradability)

no data available

Ecotoxicity effects

no data available

Further information on ecology

no data available

13. DISPOSAL CONSIDERATIONS

Product
Burn in a chemical incinerator equipped with an afterburner and scrubber but exert extra care in igniting as this material is highly flammable. Observe all federal, state, and local environmental regulations. Contact a licensed professional waste disposal service to dispose of this material.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
UN-Number: 1033 Class: 2.1
Proper shipping name: Dimethyl ether
Marine pollutant: No
Poison Inhalation Hazard: No

IMDG
UN-Number: 1033 Class: 2.1 EMS-No: F-D, S-U
Proper shipping name: DIMETHYL ETHER
Marine pollutant: No

IATA
UN-Number: 1033 Class: 2.1
Proper shipping name: Dimethyl ether
IATA Passenger: Not permitted for transport

15. REGULATORY INFORMATION

OSHA Hazards
Flammable Gas

DSL Status
All components of this product are on the Canadian DSL list.

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards
Fire Hazard

Massachusetts Right To Know Components

	CAS-No.	Revision Date
Dimethyl ether	115-10-6	1991-07-01

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Dimethyl ether	115-10-6	1991-07-01

New Jersey Right To Know Components

	CAS-No.	Revision Date
Dimethyl ether	115-10-6	1991-07-01

California Prop. 65 Components
This product does not contain any chemicals known to State of California to cause cancer, birth, or any other reproductive defects.

16. OTHER INFORMATION

Further information