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Kinetics and Deactivation in the Methanol Synthesis Reaction

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Abstract:

This study is highlighting the synthesis of methanol by using Cu-based ($Cu/ZnO/Al_2O_3$) catalyst and synthesis gas, which consists a mixture of CO, CO_2, H_2, N_2 and CH_4. The catalyst was prepared as per the procedure described by the ICI and characterized by performing X-ray diffraction and Nitrogen adsorption/desorption. Experiments were carried out for the methanol synthesis at 80 bar pressure as well as at 255ºC temperatures and found very good reproducibility. The deactivation of the prepared catalyst was studied by using laboratory based fixed bed reactor. The experimental result showed that the prepared catalyst was highly stable and there was no deactivation of the catalyst up to 240 hours of the reaction period of time. The effect of the composition of feed gas (i.e., synthesis gas) on the activation energy of methanol synthesis was measured at specific conditions of pressure and contact time. However, the maximum r_{CH_3OH} was observed whenever the ratio of H_2/CO was 2. The higher production of methanol was 2.084 g/h, which was observed at specific pressure, temperature and contact time of feed in the experiment.

I declare that this is an independent work according to the regulations of Norwegian University of Science and Technology.

Date and Signature:21/06/2011

Preface

This thesis has been prepared as a partial fulfillment of the Master of Science at the Department of Chemical Engineering, Faculty of Natural Sciences and Technology, Norwegian University of Science and Technology, Trondheim, Norway. The relevant all works in order to prepare Masters Thesis were carried out during the period of January to June 2011.

The entire work relevant to the thesis was supervised by Professor Hilde J. Venvik and co-advised by Professor Anders Holmen, Department of Chemical Engineering, Faculty of Natural Sciences and Technology, Norwegian University of Science and Technology, Trondheim, Norway.

A CD-ROM, containing all data files obtained from the experimental work is attached with the thesis.

Trondheim, June 2011

Mahmud Alam

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List of Symbols and Abbreviations

MTPD	Metric Ton per Day
MeOH	Methanol
ΔH_{298}	Change of standard enthalpy of formation at 298 K
BASF	Badische Anilin and Soda Fabrik
ICI	Imperial Chemical Industries Limited
XRD	X-Ray Diffraction
λ	Wavelength
θ	The angle between the incoming x-rays and the normal to reflecting lattice plane
η	An integer called the order of the reflection
β	Peak Width
k	rate constant
BET	Brunauer Emmett Teller
E_1	The heat of adsorption
E_L	Heat of adsorption second and higher layer
N_a	Avogadros number
V	The mole volume of adsorbent
WGS	Water Gas Shift reaction
HES	Health Environment and Safety
GC	Gas Chromatography

1 Introduction

The greenhouse effect has been recognized worldwide to be an important and critical issue and a number of countermeasures are proposed to reduce the effect of green house. The continuous emission of carbon dioxide in the air has been identified as one of the major causes of green house effect and therefore, catalytic hydrogenation of carbon dioxide to produce chemical and fuels has received much attention as one of the most promising mitigation options. In particular, methanol production by hydrogenation of carbon dioxide has been considered as a mean to reduce carbon dioxide emission, but the greater challenge is related to the availability of potential source of hydrogen [1].

The production of methanol is around 40 million tons per year in the world [2]. The production rate is increasing 4% annually. Methanol has traditionally been used as feed for production of a range of chemicals such as acetic acid (CH_3COOH) and formaldehyde ($HCHO$). In recent years, methanol is also used for synthesis of others chemical, for example, DME (dimethyl-ether) and olefins and other fuels. The most of the methanol is produced from natural gas and especially in Middle East, the industrial infrastructure have been established in areas where natural gas is available and cheap. In China, the methanol is produced from coal where natural gas is not available. There is doubt that in near future, natural gas can be used for the continuous production of methanol due to its uncertain availability [3]. The capacity of methanol industries has increased considerably during the last decade. In 1996, a world scale methanol plant with a capacity of 2500 MTPD was started up in Tjeldbergodden, Norway. However, now a day, several plants are in operation with higher capacity for methanol production throughout the world [2].

Methanol is a colourless liquid with boiling point of 65°C and it can mix with organic liquids as well as with water. Therefore, it is often used as a solvent for domestic and industrial applications. Due to its beneficial physical properties, like low freezing temperature, it is used as a refrigerant. Moreover, methanol has been used as clean fuel that produces less pollution and thus it can be considered as an important alternative fuel. The technology for commercial methanol production has been available since the early of the 20th century, considering its potential usage it is an intense research of interest for scientists to prepare better catalysts, which would enable the synthesis reaction in a cost-effective manner with sustainable production [3].

To save the earth from the energy crisis in future, technologist must pay attention to the fundamental aspects of the process design in order to improve the efficacy of the process. A small improvement in energy and process efficiency, can being a large benefit to the commercial production. The new research should emphasize the several issues related to heat and mass transfer, thermodynamics, kinetics, reactor design, modelling, process control, optimization and energy integration [3].

In the light of circumstances mentioned above, the major aim of the thesis is to prepare highly stable catalyst in order to synthesis of methanol in a cost effective manner with ensuring sustainable production. Considering the aim of this study, the major objectives of the study is to: (i) measure the deactivation of catalyst in the synthesis process of methanol, (ii) quantify the activation energy of methanol synthesis, and (iii) measure the maximum production by using the ratio of H_2/CO.

2 Methanol production in past-a brief overview

In 1923, the methanol was first produced by the BASF in Leuna, Germany. Although, in some researchers claimed that G. Partort, a French Portent, was the first inventor of methanol, who produced oxygenated hydrocarbon in 1921 by reacting a gaseous mixture of CO and H_2. In the beginning of the 20th century, in Germany, a research and development programme was initiated to produce hydrogen and synthesis gas at high pressure that are commonly known as 'Hydrerungs verfahrung'. However, such intervention led to develop the Haber-Bosch ammonia synthesis, the hydro-desulphurization process (Bergius, 1920), the Fischer-Tropsch discovery (Hans Fischer and Franz Tropsch, 1923) and the invention of methanol production from synthesis gas [4]. The development of the methanol synthesis process was started by M. Pier in February 1922 and he used the ammonia synthesis equipment of BASF [4].

Crude methanol was first produced in 1923 and at that time, the methanol had been produced from wood distillate (i.e., a pyrolysis process with low yields and intensive feed-stock handling). The high pressure process that was developed by the BASF, operated at up to 250-350 bar pressure and 320-450ºC acted as dominant technology over the last 45 years for methanol synthesis. The prior of that time, the synthesis gas produced from German coal/lignite was contaminated with chlorine and sulphur and considered as a strong catalyst poisons. Then a relatively poison resistance catalyst (ZnO / Cr_2O_3) was developed and a cupper based catalyst was applied to produce methanol, but the experiment failed to show any significant output. Later on during 1960s, the Imperial Chemical Industries (ICI) improved the use of Cu-based catalyst concept and they concluded that Zn is the perfect dispersant for Cupper and enhance the reactivity of catalyst at lower operating conditions [4].

3 Methanol synthesis

3.1 Chemistry of methanol synthesis

The catalytically conversion of synthesis gas to methanol has been commercially available since 1923 and at that time, the first commercial plant for methanol synthesis was built by the BASF. The technology of the methanol production has gone through constant improvements and major modifications, among which the biggest change was undoubtedly a transition from high-pressure synthesis to low-pressure synthesis. The production of methanol is the heterogeneous catalytic conversion of synthesis gas that originates from natural gas or coal. The composition of synthesis gas varies widely, depending on the process of conversion as well as the type of feed stocks [5].

3.2 Conversion of synthesis gas to Methanol

The synthesis gas is a mixture of hydrogen, carbon dioxide, carbon monoxide as principle components and consist methane and steam as secondary components. The synthesis gas is typically produced via steam reforming of natural gas, gasification or partial oxidation of coal, gasification of bio-mass, gasification of municipal solid wastes, coke oven gas etc. The most popularly used commercial catalyst is $CuO/ZnO/Al_2O_3$ which is synthesized by co-precipitation process. In such a catalyst formulation, alumina (Al_2O_3) is a support that can be replaced by other similar support, for example, ThO_2. The major stoichiometric reactions involved in the commercial conversion to produce methanol are mentioning bellow:

$$CO_2+3H_2=CH_3OH+H_2O \qquad \Delta H_r = -90.8 \text{ KJ/mol} \qquad (3.2.1)$$

$$CO+2H_2= CH_3OH \qquad \Delta H_r = -49.6 \text{ KJ/mol} \qquad (3.2.2)$$

$$CO+ H_2O= CO_2+ H_2 \qquad \Delta H_r = -41.0 \text{ KJ/mol} \qquad (3.2.3)$$

Both of reaction (3.2.1) and (3.2.2) are exothermic and resulting in a reduction in volume. The conversion reaction is, therefore, favored by low temperature and high pressures. Today's synthesis process is done at low pressure, some even close to the pressure at which the steam reforming production of synthesis gas operate. So this process consumes less energy than the high pressure ones as the synthesis gas compression is a costly operation [5].

4 Methanol synthesis catalyst

The first commercial plant of methanol synthesis was build by the BASF in 1923 and ZnO/Cr_2O_3 was used as catalyst, which operated at 300ºC and 200 atm pressures. After that, the process was successfully operated over a long period of time and later that process was replaced by more efficient and low pressure methanol synthesis technology. In 1927, the Commercial Solvent Corporation and DuPont were started the experiment for methanol synthesis and in the same year, DuPont established a commercial plant at Belle to produce methanol and ammonia by using coal as a raw material, while ZnO/Cr_2O_3 or Cr_2O_3/CuO was used as catalyst [3].

The first patent for methanol synthesis on cupper based catalysts was reported in 1921 by Patart [4], but due to low thermal resistance of this catalyst it was not used as commercially approximately for half a century. It was also suspected that the sulphur poisoned the cupper based catalyst. When ICI was developed a process to produce synthesis gas almost free of impurities by steam reforming of naphtha, the use of copper based catalysts was received much attention for methanol synthesis process (Humphreys et al. 1974), The modern ICI methanol process was developed initially based on ternary catalysts containing CuO, ZnO and Cr_2O_3 under 250-270 ºC at 50-100 bar pressure. However, another study indicated that the alumina rather than Cr_2O_3 increased life time of catalyst and therefore, low-pressure catalyst contain alumina as a third components rather than Cr_2O_3 [7]. Now a day, there are several catalysts allowing the production of almost pure methanol from synthesis gas under the low pressure (< 100 atm). These catalysts are containing cupper and a mixture of oxides such as ZnO - Al_2O_3 or ZnO $-Cr_2O_3$. Other oxides have also been used as catalyst support [8].

4.1 Cu/ZnO-Al_2O_3 catalysts

The $Cu/ZnO/Al_2O_3$ catalyst is widely used in the commercial process plant of methanol synthesis and Cr_2O_3 based catalyst also found to be used in commercial production of methanol [9]. The $Cu/ZnO/Al_2O_3$ catalyst is very active for CO rich feed, but the activeness of this catalyst decreased with increasing the amount of CO_2 in the feed [10]. However, the utilization of CO_2 is typically important due to environmental regulations and thus many studies have been carried out in order to find a catalyst that is active with CO_2-rich feed. Therefore, Cu-based catalyst has been studied with metal additives [10].

The Cu/ZnO catalyst performs well with CO rich feed, but the loss of activity in the CO_2 rich feed occurred due to the presence of water, which is produced along with methanol in CO_2 hydrogenation [11]. Water is also identified as a responsible one to decrease the action of $Cu/ZnO/Al_2O_3$ observed in another study [12]. By using different feed compositions, it was observed that the methanol yield decreases and water yield increases with increasing the rate of CO_2 in feed, and the presence of water accelerated the deactivation of the Cu/ZnO-based catalysts and added silica into the catalyst can slow down the effect of water and allow the methanol synthesis from the CO_2-rich feed [13]. Cu/ZnO catalysts with alcohol promoters (such as ethanol, propanol and buthanol) at low pressure (i.e., 3.0 MPa) and 443K for methanol synthesis has also been reported, the reaction at low temperature led to high conversion of CO from 50% to 80 % [14]. The influence of Zn, Cr and Co oxide additives were tested into Cu-based catalysts and observed significant improvements in the catalyst activities that increases the water gas shift reaction in methanol synthesis. No significant changes in activity were observed when CoO [15] added. Nevertheless, SiO_2 and its influence to the activity of the Cu-based catalysts have been studied [16] and the addition of SiO_2 increased the catalytic activity for the methanol synthesis from CO_2 [17].

4.2 Catalysts with Zirconium (Zr)

It has been recognized that Zirconium is one of the potential support materials to Cu-based catalysts, since it has improved the activity of catalysts for methanol synthesis from both CO and CO_2 [18]. Manganese (Mn) promoted Cu/Zn/Zr catalysts have been investigated and compared with $Cu/ZnO/Al_2O_3$ catalyst showed that zirconium influenced the catalyst activity and whenever added Mn to Cu/Zn/Zr catalyst that increased the rate of methanol production [19]. In addition, it was observed that Mn promoted cupper/zinc/zirconia catalyst exhibited remarkable high stability and high selectivity although crude methanol did not contain any by-products other than water [19].

Comparing the use of Cu, Ag and Au in the catalysts (M/ (3ZnO/ZrO_2) for methanol synthesis, where M denoted as Cu, Ag or Au, the catalyst with Cu showed the highest activity in methanol synthesis [20]. But in the case of Cu/SiO_2 catalyst with Zr increased the rate of methanol synthesis with increasing the load of Zr [16]. The comparison study between Cu/SiO_2 and $Cu/ZrO_2/SiO_2$ in the hydrogenation of CO revealed that the rate of methanol synthesis is enhanced when Zr added in the catalyst [21] and the evaluation of the same catalysts with Ti in the experiment indicated that the addition of Ti has similar influence as Zr [22]. However, to test the influence of adding Ce to ZrO_2, it was found that $Cu/Ce_xZr_{1-x}O_2$ catalysts varying with Ce content and the adding Ce increased the activity of the catalyst for methanol synthesis through hydrogenation of CO_2 [23]. The promoting action of Ga oxide to the catalyst for methanol synthesis from CO_2 was investigated based on $Cu/ZnO/ZrO_2/Al_2O_3$ and $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$ catalysts and the findings of this study concluded that the activities of these catalysts were higher than the activities of the traditional Cu-based catalysts [11].

4.3 Pd-based catalysts

At high temperature, the deactivation of Cu/ZnO catalyst occurs quickly in methanol synthesis reaction but Pd supported Cu-based catalyst shows more stability [24]. The preparation methods that influence to obtain best structure of Pd-ZnO catalysts was studied [25]. The influence of different oxide additives to supported Pd catalyst was also tested and the outcomes of this research proved that the catalyst of Pd supported by CeO_2 showed more activity and long lifetime for methanol synthesis from CO_2 similar as La_2O_3 and TiO_2 [26]. The comparison between Cu-based catalyst and Pd-based catalyst in presence of Ce in both catalysts exhibited that Cu-based catalyst equally performed similar as Pd-based catalyst [27].

4.4 Other Catalyst

Methanol synthesis from CO by using Cu-based catalyst with potassium (K) conformed that the K acts as a promoter during the methanol production when prepared catalyst was selective for methanol synthesis, although CO_2 had a negligible effect on the performance of the catalyst to the applied pressure regime [28].

5 Methanol synthesis technologies

The systematic synthesis of methanol has a history of about 100 years dating back to the early 1900’s, when methanol was produced from destructive distillation of wood and thus known as wood alcohol. In 1923, the BASF developed a high pressure catalytic commercial methanol synthesis process operated at 250 to 350 atm pressures and ever since, the high pressure methanol technology was adopted popularly by a number of industries almost 50 years. In 1963, ICI developed a low pressure methanol synthesis process, which was operated at 50 to 100 atm pressures [3].

5.1 The Conventional ICI’s 100-ATM methanol Synthesis Process

In the mid-1900’s, ICI reduced the methanol synthesis pressure by using catalyst but the process was not ideal for large capacity of production unit due to the necessity of large equipment under low pressure condition which ultimately caused slower rate of reaction. Then the effort was made to find out better materials and equipment design as well as search for a suitable catalytic system that would be more active at 100 atm pressure. As a consequent of such initiative in 1972, ICI recommended $Cu/ZnO/Al_2O_3$ catalyst system that ultimately enhanced and bring modification in the designing of energy efficient process as well as the optimization process. A process diagram is given in bellow. Along with efficient design, management of catalyst life has always been the principle issue of the process maintenance and enhancement [3].

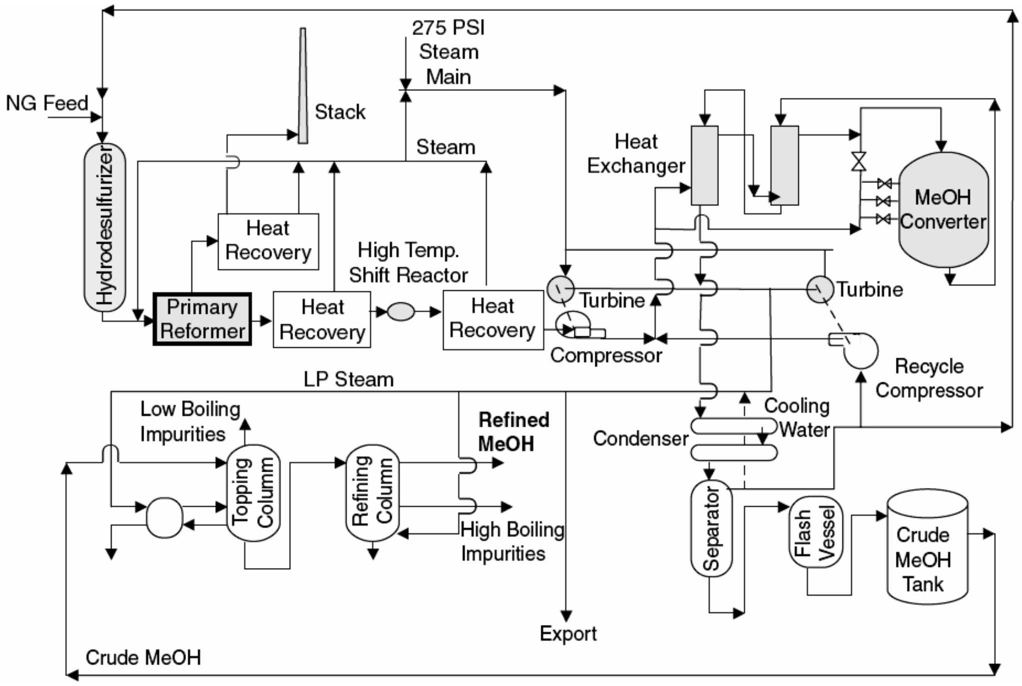


Figure 5-1 A schematic of ICI’s Low-Pressure methanol synthesis process [3]

5.2 Haldor Topsoe A/S Low-Pressure Methanol Synthesis Process

This process is designed to produce methanol from natural or associated gas feed stocks, utilizing a two-step reforming process to generate feed synthesis gas mixture for the methanol synthesis. Associated gas is a natural gas produced with crude oil from the same reservoir. It is claimed that the total investment for this process is lower than the conventional flow scheme which based on straight steam reforming of natural gas approximately 10%, even after considering an oxygen plant [29]. The two-stage reforming usually conducted by primary reforming, in where, a preheated mixture of natural gas and steam are reacted and in the secondary reforming stage, the exit gas further converted with the aid of oxygen. The energy integration process was done as shown in Figure 5-2 in bellow. The process technology is suitable for smaller to larger methanol plants up to 10,000 TPD [3].

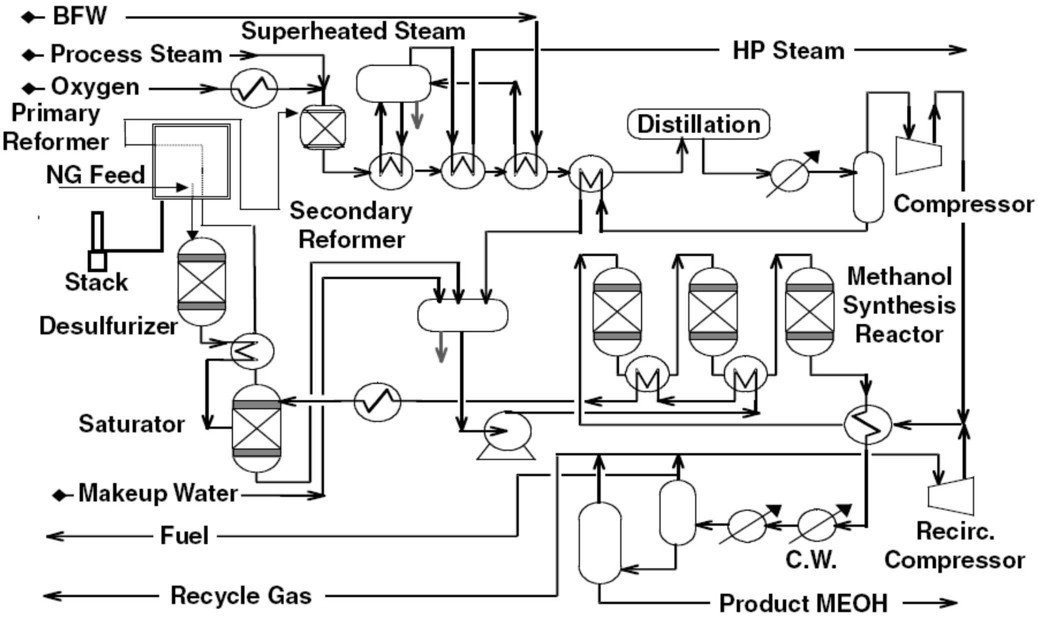


Figure 5-2 A schematic of Haldor Topsoe A/S Low-Pressure methanol synthesis process [3].

5.3 Kvaerner Methanol Synthesis Process

This process was developed by the Kvaerner Process Technology/Synetix, UK based on a low-pressure methanol synthesis process and two-stage steam reforming, similar to the Haldor Topsoe process. Figure 5-3 shows a schematic of the Kvaerner methanol synthesis process. The feed gas stock may be natural or associated gas. In this process, however, carbon dioxide can be used as a supplementary feedstock in order to adjust the stoichiometric ratio of the synthesis gas. However, this process is more suitable for regions with high availability of low-cost gas such as CO_2 - rich natural gas and financial restrictions of low capital investment. There are a number of commercial plants currently in operation based on this design and their typical sizes range from 2000 to 3000 MTPD [6].

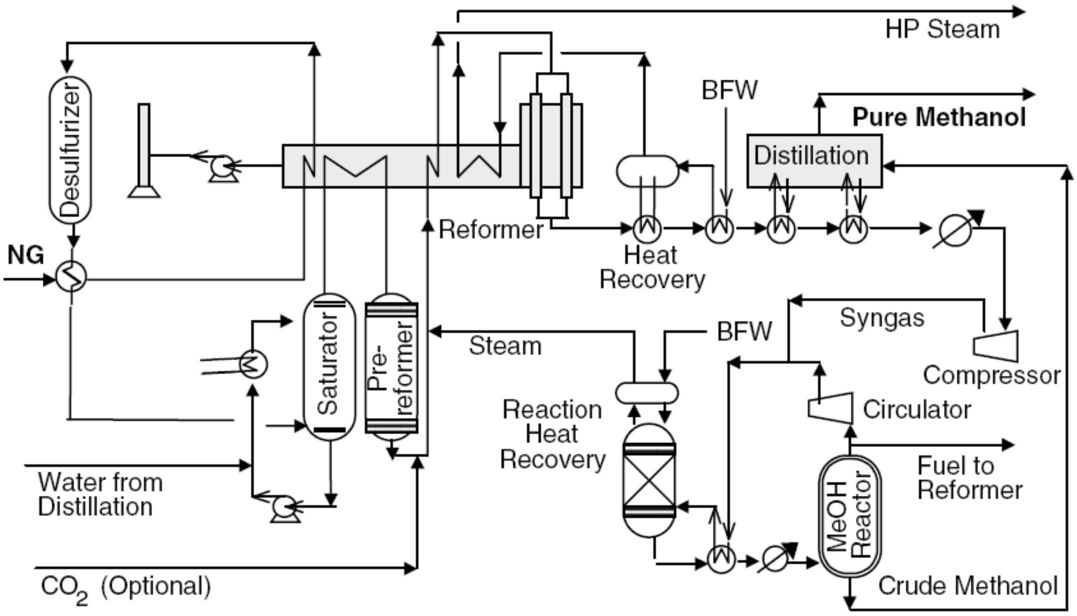


Figure 5-3 A schematic of Kvaerner Low-Pressure methanol synthesis process [6].

5.4 Krupp Uhde's Methanol Synthesis Process

The process, developed by Krupp Uhde GmbH based on the low-pressure synthesis process of methanol as well as steam reforming for synthesis gas generation. A unique feature of this process is its flexibility of feedstock choice, which includes natural gas, liquefied petroleum gas, or heavy naphtha [29]. The steam reformer is uniquely designed with a top fired box type furnace with a cold outlet header system. The steam reforming reaction usually takes place heterogeneously over a nickel catalyst system. The reformer effluent gas that contain H_2, CO, CO_2, and CH_4 are allowed to cool from 880°C to ambient temperature eventually, and most of the heat content is recovered by steam generation, BFW preheating, preheating of demineralized water, and heating of crude methanol for three-column distillation. Eleven plants have been built until 2005 using such technology. Figure 5-4 showing a schematic of Krupp Uhde's methanol synthesis process [29].

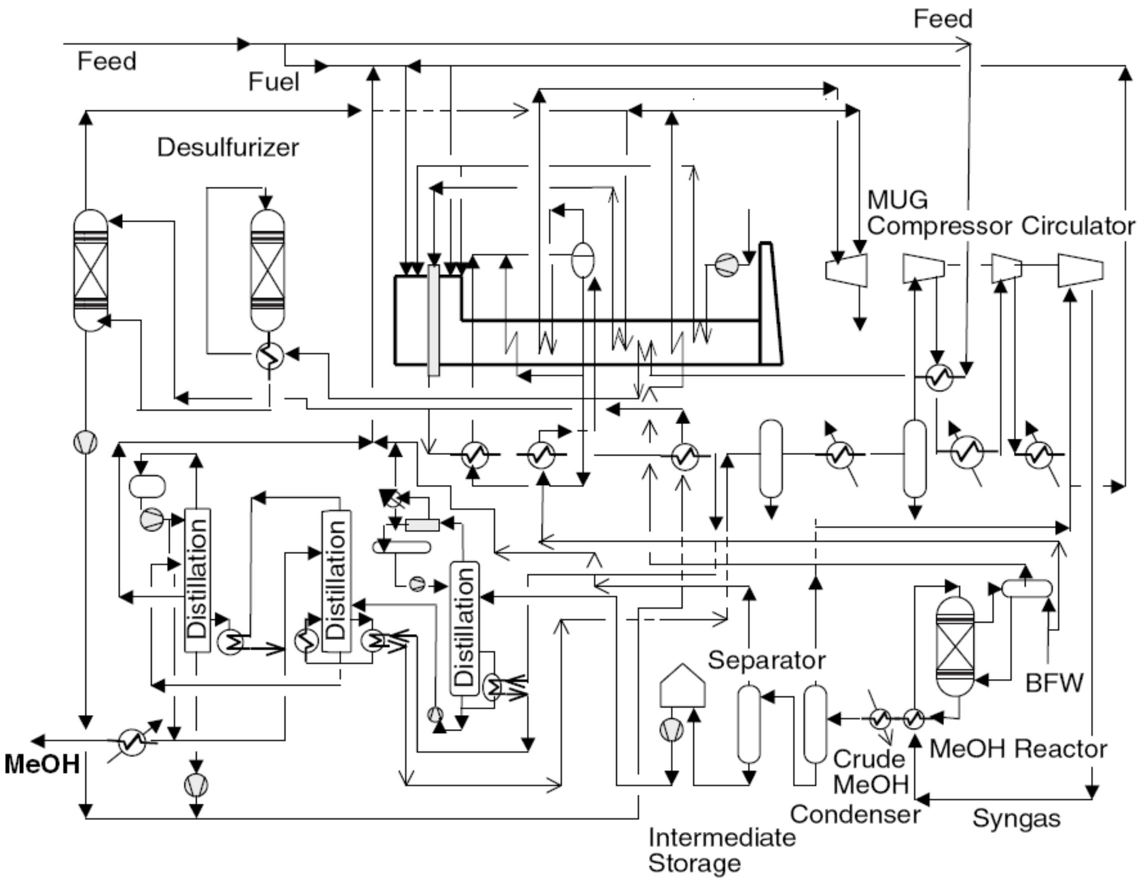


Figure 5-4 A schematic of Krupp Uhde methanol synthesis process [29].

6 Thermodynamic of methanol Synthesis

Normally methanol is synthesized by catalytic hydrogenation of CO.

$CO+2H_2= CH_3OH$ ΔH_r = -91.07 KJ/mol ………... (6.1)

Two more reactions are taken place during the methanol production process as mentioned in bellow:

$CO_2+3H_2=CH_3OH+H_2O$ ΔH_r =-52.8 KJ/mol……………. (6.2)

$CO_2+3H_2= CO+ H_2O$ ΔH_r = -41.12 KJ/mol…………. (6.3)

All the above reactions are reversible and exothermic, produce heat during the reaction. The equation 6.3 is known as Water Gas Shift reaction. Moreover, the reactions are exothermic and reduce in the volume of product. The higher yield of methanol is obtained at high pressure and low temperature [30].

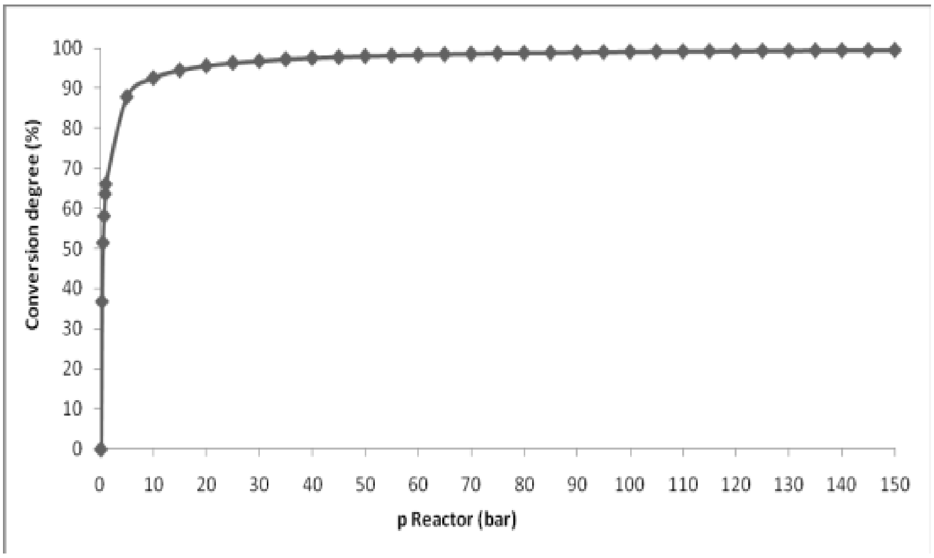


Figure 6-1 Degree of Conversion of CO against Reaction Pressure at 25ºC [30].

As seen in Figure 6-1, degree of conversion of CO is increased with increasing of pressure, but for pressure higher than 10 bar the conversion degree is 90% or greater, and for p=80 bar almost an overall conversion is reached [30].

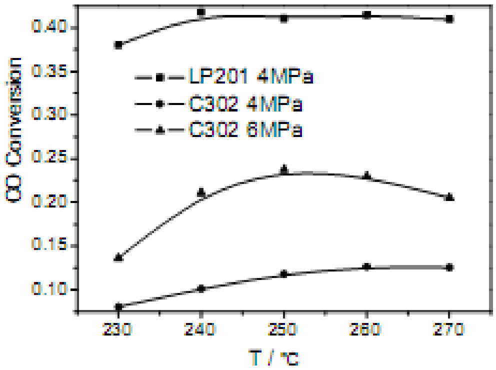


Figure 6-2 the comparison of the activities of Liquid phase LP201 and C302 at a space velocity of 3000 $ml / g_{cat}.h$ [31].

The activities of the LP201 (a new catalyst denoted LP201) and commercial C302 (manufactured in China) catalysts in a mechanical agitated slurry reactor are compared. The result is shown in Figure 6-2. It can be seen that the activity of the LP201 catalyst is much higher than that of the commercial C302 catalyst. When LP201 is used, its synthesis gas conversion at the lower pressure of 4 MPa is higher than that of C302 at 6 MPa. This indicates that the LP201 catalyst is suitable for the large scale synthesis of methanol in a slurry reactor [31].

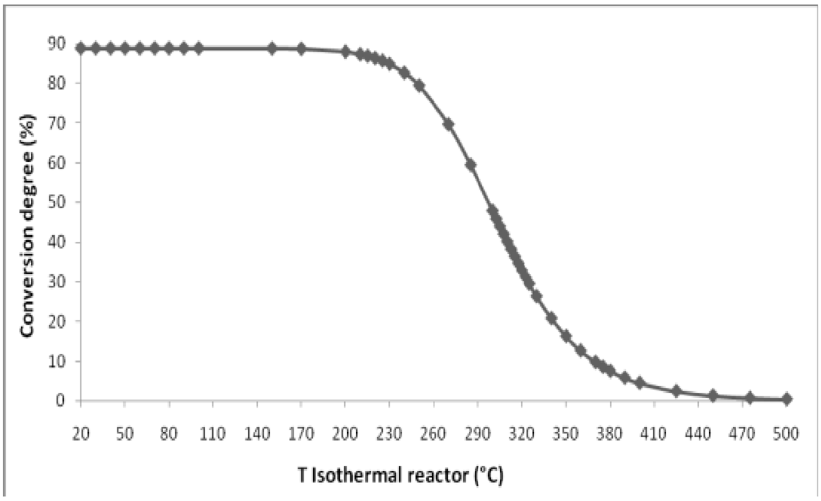


Figure 6-3 Degree of Conversion of CO against Reaction Temperature at 80 bar pressure [30].

When the reactor temperature is increased the corresponding decrease of conversion grade is observed (Figure 6-3). In accordance with thermodynamic data, low reaction temperatures provide high conversion grades. Definitely, in an isothermal reactor the excess reaction heat have to be removed through a proper exchange [30].

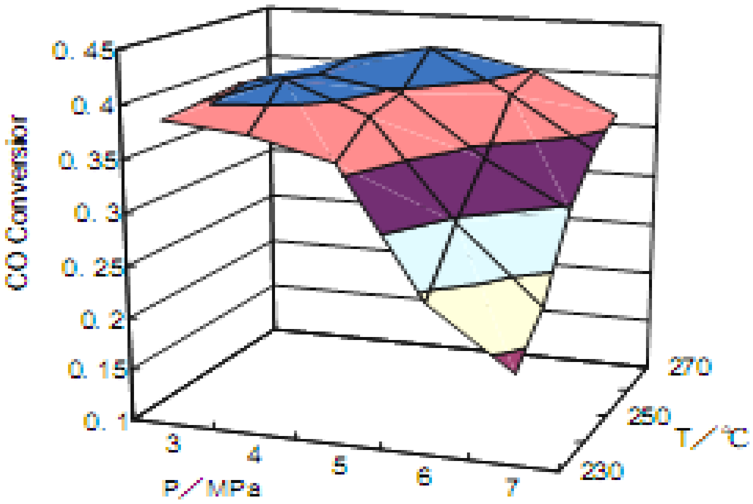


Figure 6-4 Influence of temperature and pressure on CO conversion at a space velocity of 3000 $ml / g_{cat} .h$ **[31].**

Figure 6.4 shows the influence of temperature and pressure on CO conversion in a slurry reactor. There exist different phenomena at high and low pressure conditions. When the pressure is relatively low, with an increase in temperature, the change in CO conversion is not monotonic, and the trend is that of an increase followed by a decrease, with the maximum conversion appearing near 250 ºC.

7 Kinetics of Methanol Synthesis

7.1 Rate expiration of methanol synthesis

The commercial productions of methanol have been started since 1923, but still there are open question about the mechanism and kinetics of methanol synthesis reaction [32]. The mechanisms for the catalytic conversion of $CO/CO_2/H_2$ feed into methanol over the catalyst $Cu/ZnO/Al_2O_3$ are well known and a number of kinetics equations have been proposed. The mechanisms are based on the following reactions [33].

$CO_2+3H_2=CH_3OH+H_2O$ ………………………………………………………… (7.1.1)

$CO+2H_2= CH_3OH$ ……..……………………………………………………….. (7.1.2)

Here K_1^* and K_2^* are the equilibrium constants for reaction 7.1.1 and 7.1.2

The water gas shift reaction is

$CO+ H_2O= CO_2+ H_2$…………………………………………………………… (7.1.3)

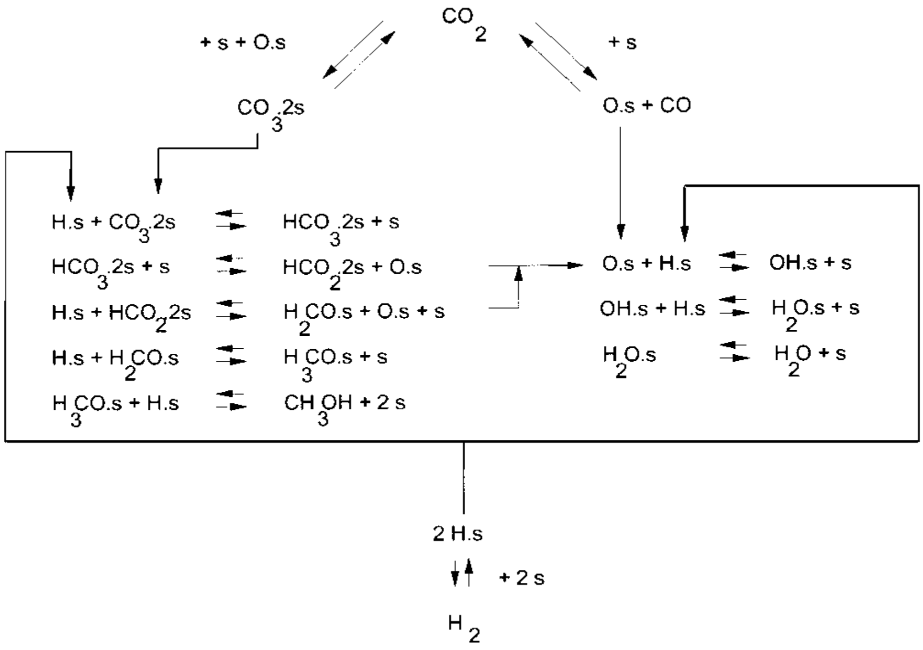


Figure 7-1 the reaction scheme for the synthesis of methanol and water gas shift reaction [33]

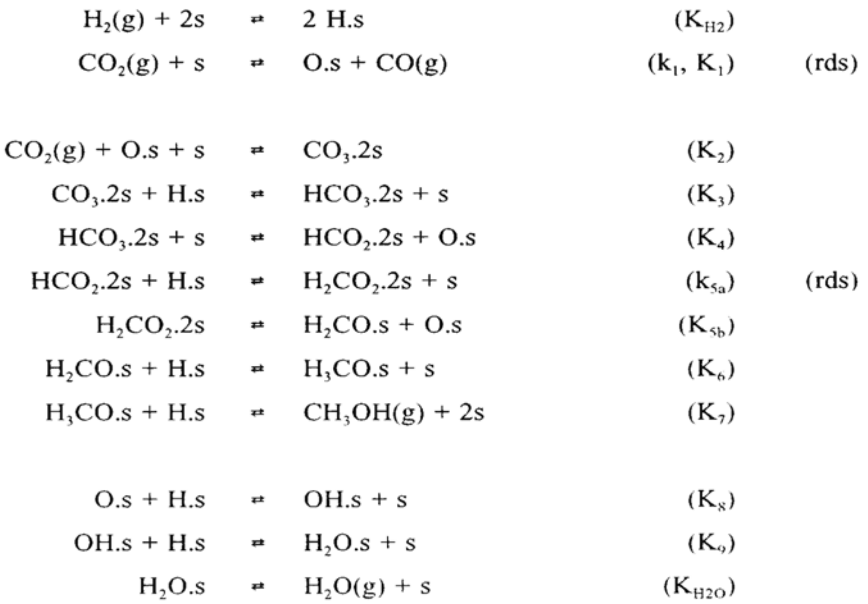


Figure 7-2 the reaction scheme for the synthesis of methanol and reverse water gas shift reactions. rds, rate determining step [33].

The value of K_1^* and K_3^* are taken from Graaf et al (1986) [34].

$$\log_{10} K_1^* = \frac{3066}{T} - 10.592 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad (7.1.4)$$

$$\log_{10} 1/K_3^* = \frac{-2073}{T} + 2.029 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7.1.5)$$

Here T in K [34].

According to Graaf et al (1986) [34], the kinetics expression for methanol synthesis and water gas shift reaction as in below:

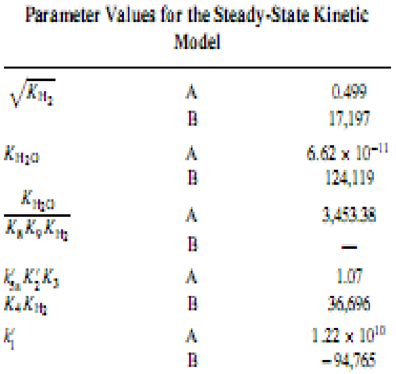
Model A:

$$r_{CH_3OH} = \frac{K_{5a}^{'}K_2^{'}K_3K_4K_{H_2}P_{CO_2}P_{H_2}[1-\frac{P_{H_2O}P_{CH_3OH}}{P_{H_2}^3P_{CO_2}K_1^*}]}{(1+(\frac{K_{H_2O}}{K_8K_9K_{H_2}})(\frac{P_{H_2O}}{P_{H_2}})+\sqrt{K_{H_2}P_{H_2}}+K_{H_2O}P_{H_2O})^3}$$

Model B:

$$r_{RWGS} = \frac{K_1^{'}P_{CO_2}[1-K_3^*(\frac{P_{H_2O}P_{CO}}{P_{CO_2}P_{H_2}})]}{(1+(\frac{K_{H_2O}}{K_8K_9K_{H_2}})(\frac{P_{H_2O}}{P_{H_2}})+\sqrt{K_{H_2}P_{H_2}}+K_{H_2O}P_{H_2O})}$$

Here pressure in bar and reaction rates in mol/Kg cat.-s [35]



Parameter Values for the Steady-State Kinetic Model

$\sqrt{K_{H_2}}$	A	0.499
	B	17,197
K_{H_2O}	A	6.62 x 10^{-11}
	B	124,119
$\frac{K_{H_2O}}{K_8K_9K_{H_2}}$	A	3,453.38
	B	—
$K_{5a}K_2'K_3$	A	1.07
$K_4K_{H_2}$	B	36,696
K_1'	A	1.22 x 10^{10}
	B	−94,765

Figure 7-3 Parameter Values for the steady state kinetic model [34].

7.2 Activation energy of methanol synthesis

For measurement of kinetics study, the experiment is carried out at a study-state conditions and external mass and heat transfer limitations are always negligible. In fixed bed reactor, the rate is evaluated by the numerically solving of mass balance equation. According to Graaf et al 1988[35], assuming the equation 7.1.2 reaction is rate controlling step for methanol synthesis, the kinetics rate expiration can be written as in bellow [36].

$$r_{CH_3OH(CO)} = \frac{K'K_{CO}[f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / (f_{H_2}^{1/2} K_{eq}^0)]}{(1+K_{CO} f_{CO} + K_{CO_2} f_{CO_2})(f_{H_2}^{1/2} + (K_{H_2O} / K_{H_2}^{1/2}) f_{H_2O})} \text{……………………. (7.2.1)}$$

Here, f_i is fugacity of particular gas [36].

This simplification equation is obtained by assuming the first order reaction. It is already assume that the methanol is formed from CO and water adsorption is almost negligible and adsorption of CO is predominated then $f_{H_2}^{1/2} > (K_{H_2O} / K_{H_2}^{1/2}) f_{H_2O}$ and $K_{CO} f_{CO} > 1 + K_{CO_2} f_{CO_2}$ [37]. So the equation 7.2.1 become as

$$r_{CH_3OH(CO)} = K(f_{H_2} - \frac{f_{CH_3OH}}{f_{CO} f_{H_2} K_{eq}^0}) \text{……………………………………………….. (7.2.2)}$$

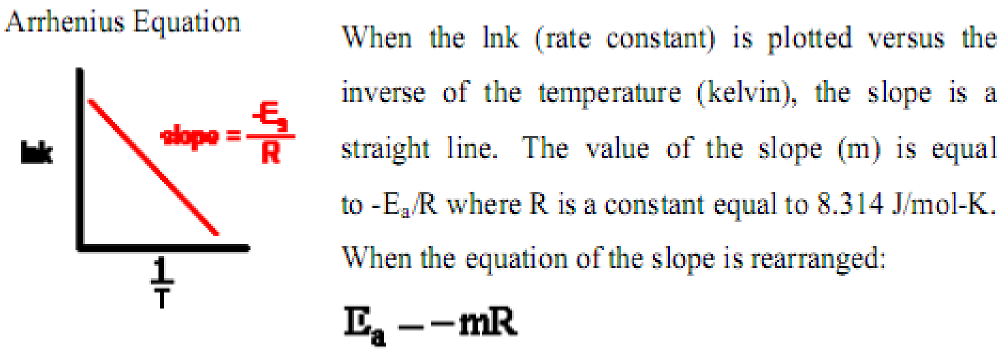
The fugacity of gas mixture can be replaced by partial pressure of gas mixture

$$r_{CH_3OH(CO)} = K(P_{H_2} - \frac{P_{CH_3OH}}{P_{CO} P_{H_2} K_{eq}^0}) \text{……………………………………………... (7.2.3)}$$

According to Arrhenius,

$$k = k^0 \exp(\frac{-E_a}{RT}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7.2.4)$$

$$\ln k = \ln k^0 - \frac{-E_a}{RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7.2.5)$$



When the lnk (rate constant) is plotted versus the inverse of the temperature (kelvin), the slope is a straight line. The value of the slope (m) is equal to -E_a/R where R is a constant equal to 8.314 J/mol-K. When the equation of the slope is rearranged:

$$E_a = -mR$$

Figure 7-4 the lnk is plotted versus the inverse of the temperature.

7.3 The order of reaction

The power rate law can be expressed as in below

$$r = kP_A^{n_A} P_B^{n_B} P_C^{n_C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7.3.1)$$

If we consider that the methanol formation is taken place according to the reaction 7.1.2, the power rate low can be written as

$$r = kP_{H_2}^{n_{H_2}} P_{CO}^{n_{CO}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7.3.2)$$

Or

$$\ln r = \ln k + n_{H_2} \ln P_{H_2} + n_{CO} \ln P_{CO} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7.3.3)$$

Here n_{H_2} is the order of reaction with respect to H_2 , n_{CO} is the order of reaction with respect to CO and k is known as rate constant [39].

8 Synthesis Gas for Methanol

Methanol is produced from the catalytic reaction of synthesis gas. The composition of synthesis gas has great influenced on the production of methanol. The stoichiometry for methanol synthesis from synthesis gas as in given below [38].

$$M = \frac{H_2 - CO_2}{CO + CO_2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots... (8.1)$$

Here, M is stoichiometric number [38].

The value of M required for methanol synthesis is 2 but commercially desirable value of S_N is 1.95 to 2.15 [38].

Normally the most of synthesis gas is produced by steam reforming of natural gas. As shown, the reaction 7.1.1 and 7.1.2 are involved in methanol synthesis reaction. It should be desirable to minimize the amount of CO_2 in the synthesis gas for several reasons. According to reaction 7.1, the low content of CO_2 in synthesis gas, results more reactive mixture and the % of CO_2 should be at least about 2%. Moreover less % of CO_2 in synthesis gas, lower consumption of hydrogen and less production of water in methanol synthesis process. The production of methanol with lower content of water can eliminate the distillation process of crude methanol [38].

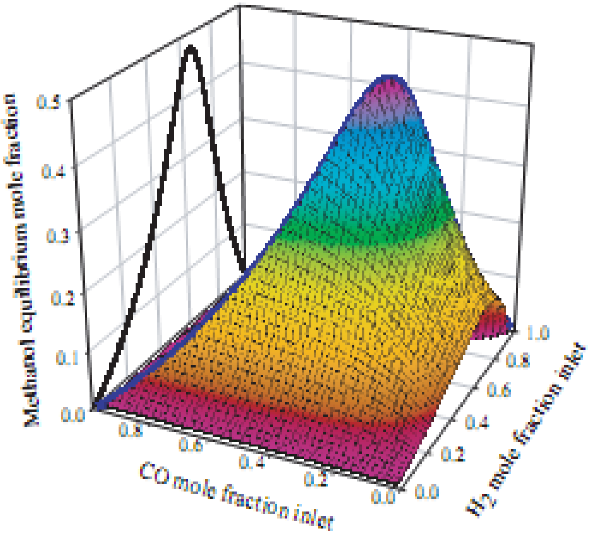


Figure 8-1 outlet equilibrium methanol concentration as function of the inlet mole fraction of H_2, CO and CO_2.

Notice that the highest methanol concentration is for a mixture of only H_2 and CO at a ratio of 2:1 (stoichiometric ratio). The solid curve is the methanol equilibrium without CO_2 in the gas mixture [40].

As shown in Figure 8-1, the maximum amount of methanol is obtained when synthesis gas contain only a pure mixture of hydrogen and carbon-monoxide. On the principle, the maximum amount of methanol can be produced from mixture of hydrogen and carbon-monoxide with minor amount of CO_2 and it should be noted that methanol is produced from CO_2 not from CO [40].

The composition of synthesis gas depends on the feedstock from which it is produced. When naphtha is used as feedstock, the stoichiometry ration is approximately right but when methane is used as feed, it produces excess of hydrogen. This excess hydrogen can be minimized either burn as fuel or can be added carbon dioxide with synthesis gas [41].

9 Characterization of catalyst materials

The characterization of catalyst is one of the most important fields of study in catalysis process. In the heterogeneous catalyst, the metal particles are dispersed on the support materials and activity, selectivity and stability of catalyst depend on the size of metal and size distribution in the crystalline structure of catalyst. Therefore, the studies of these parameters are the major tasks for the researcher and this process is known as catalyst characterizations [39].

9.1 X-ray diffraction

X-ray diffraction (XRD) is one of the most used techniques in catalyst characterization and it is applied to measure the crystalline phase inside the catalyst by using lattice structure parameters and getting the idea about particle size identification. When X-ray is passing through a crystalline material, the patterns produce information about size and shape of unit cell [39].

In XRD, the source of X-ray is known as x-ray fluorescence and it is consist of a target and an anode that is bombarded with high energy electrons emitted from a cathode. As a result, the anode emits x-ray from two processes. Firstly, the electrons in K-shell are emitted by the electron beam from the cathode and create a continuous background spectrum of bremsstrahlung. Thereafter, the core hold in K shell and filled up by transition of electrons which reduce the higher energy levels of L and M shells. This process lead to generation of X-ray photons [40].

XRD occurs in the elastic scattering of x-ray photons by atoms in a periodic lattice. The scattered monochromatic x-rays that are in phase give constructive interference. In catalyst, there is a 3D periodic lattice arrangement of atoms that allow each set of atom planes to form diffracted beams. From diffraction of x-ray in these crystals the space between the planes can be determined using Bragg's law as shown in equation 9.1.1. The lattice spacing determined from Bragg's law are characteristic for a certain compounds [40].

$$\mathbf{n\lambda = 2d} \sin\theta \; ; \; n=1, 2, \ldots \qquad (9.1.1)$$

Where, λ is the wavelength of X-rays, 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 and n is an integer called the order of the reflection.

In practice, the x-ray diffraction pattern of a powered sample can be measured with a stationary x-ray source and a movable detector. The intensity of diffracted radiation is then scanned as function of angle 2θ between the incoming and the diffracted beams. This setup enables to determine of the lattice spacing's and consequently crystallographic phases present in the crystal. Also particles size can be estimated from XRD patterns. The crystal size is related to peak width and can be measured by the Scherrer formula as mentioned below: [40]

$$\langle L \rangle = \frac{k\lambda}{\beta \cos\theta} \quad \text{...} \quad (9.1.2)$$

In this equation, $\langle L \rangle$ is a measurement for the dimension of the particles in the direction perpendicular to the reflecting plane, k is a constant, λ is the X-ray wavelength, β is the peak width and θ is the angle between the beam and the normal to the reflecting plane.

For catalyst characterization, XRD can provide clear and unequivocal structure information on particles (size and shape), which are enough large for XRD analysis. XRD has a limitation that it cannot detect particles either too small or amorphous [40].

9.2 Nitrogen adsorption/desorption

BET is a famous theory for physical adsorption of gas molecules on a solid surface and it is very useful technique to determine the specific surface area of material. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published the BET theory for the first time. BET consists of the first initials of their family names [42]. This theory is the extension of the Langmuir theory which is based on the theory of monolayer adsorption and BET theory is based on the multi-layer adsorptions and consist the following hypotheses: (i) gas molecules physically adsorb on a solid in layers infinitely; (ii) there is no interaction between each adsorption layer; (ii) the Langmuir theory can be applied to each layer.

BET expressed an equation as in following:

$$\frac{1}{V[(P_0/P)-1]}=\frac{C-1}{V_mC}\left(P/P_0\right)+\frac{1}{V_mC}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

(9.2.1)

Here P_0 and P are the equilibrium and the saturation pressure of the adsorbate at the temperature of adsorption, V is the volume adsorbed , V_m is the volume of the monolayer and C is the BET constant which is expressed as

$$C=\exp\left(\frac{E_1-E_L}{RT}\right)\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ (9.2.2)$$

Where E_1 the heat of adsorption for 1st is layer and E_L is for second and higher layer. This equation is the based on heat of liquefaction [42].

The BET adsorption isotherm based on the equation (9.2.1) as in below

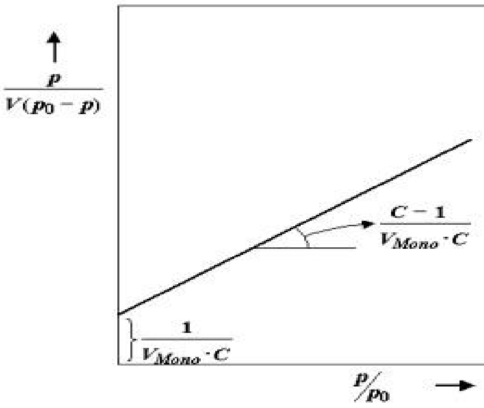


Figure 9-1 BET Adsorption Isotherm [*42*]

The value of slope A=$\frac{C-1}{V_mC}$ and intercept I=$\frac{1}{V_mC}$ of the line are used to calculate the monolayer adsorption V_m and constant C.

$$V_m=\frac{1}{A+I}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (9.2.3)$$

$$C=1+\frac{A}{I}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (9.2.4)$$

The BET is widely used in surface science for the calculation of surface area of solid by physical adsorption of gas molecules [43].

$$S_{BET.Total}=\frac{V_mN_aS}{V}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (9.2.5)$$

$$S_{BET} = \frac{S_{BET.Total}}{a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad (9.2.6)$$

Here N_a= Avogadro’s number, V= The mole volume of adsorbent gas, a= the mole weight of adsorbed [43].

10 Experimental

10.1 Methanol Synthesis Catalyst

10.1.1 Catalyst Preparation

There are many methods for preparation of Cu-based mixed oxide catalysts. In this sub-chapter, the preparation of Cu-based ($CuO/ZnO/Al_2O_3$) catalyst that was prepared by 2-steps co-precipitation followed by ICI procedure is descript in the Figure 10-1 in bellow [43].

The chemicals that are used for the synthesis of ICI methanol catalyst are below:

Table 10-1: the chemicals that are used for the synthesis of ICI methanol catalyst

Name of Chemical	Chemical Formula
Compound	
Sodium Aluminate	$NaAlO_2$
Nitric acid	HNO_3
Zinc Nitrate Tetrahydrate	$Zn(NO_3)_2.4H_2O$
Sodium Carbonate	Na_2CO_3
Cupric Nitrate Trihydrate	$Cu(NO_3)_2.3H_2O$

N.B: De-ionized water is used for preparation of catalyst.

10.1.2 Catalyst Characterization

The prepared ICI methanol catalysts were characterized by XRD and BET.

10.1.2.1 X-ray diffraction

The XRD were studied for fresh Catalyst, reduced catalyst and used catalyst powder that was shown in Figure 12-1.The X-ray patterns of catalyst were obtained using a D8 Focus diffractometer from Bruker AXS with CuKα-radiation. The D8 Focus apparatus was equipped with a 2 theta/theta gonimeter and a Lynx Eye detector. The rotation was activated.

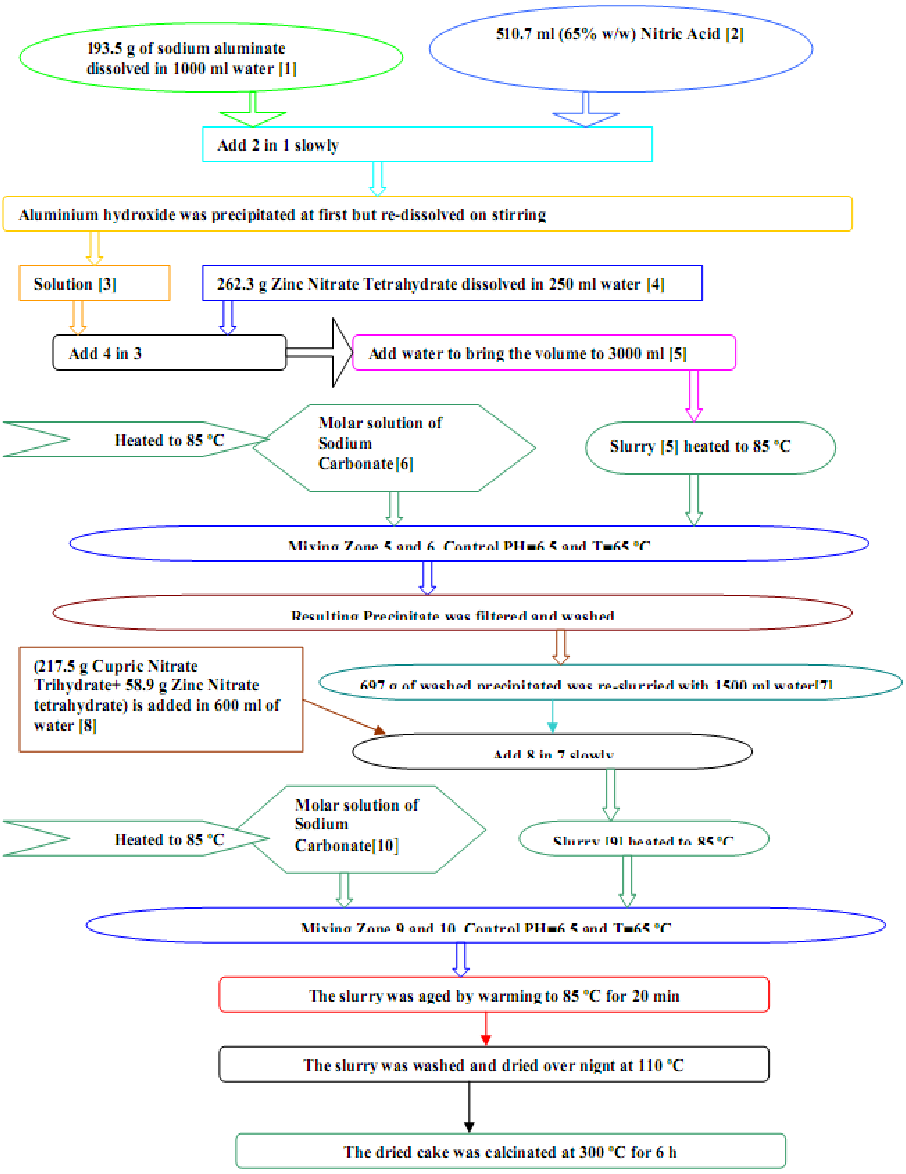


Figure 10-1 a scheme of the synthesis of methanol catalyst

10.1.2.2 Nitrogen Adsorption/Desorption

BET surface area of Cu-based catalyst that was measured, recorded in the micrometrics TriStar 3000 instrument (surface area and porosity analyzer). This experiment was performed by PhD student Xuyen Kim Phan. The amount of catalyst placed on the sample holder was approximately 0.0476 g. The catalyst was outgassed at 300 ºC around 6 hours and then it was analyzed by BET instrument.

10.1.3 Catalyst Reduction

The catalyst reduction (before reaction) was done in tubular fixed bed reactor and this process was performed around 17 hours.

In catalyst reduction process, first the fixed bed reactor was filled with 1gm (around) catalyst and then it was joined with gas flow line. A thermo well and a thermocouple were placed in the fixed bed reactor and reduction was carried out with the flow of synthesis gas containing the composition $CO : CO_2 : H_2 : N_2 = 25 : 5 : 65 : 5$. The temperature of fixed bed reactor was controlled by Eurotherm temperature controller and a Kanthal oven. A programmed was set in Eurotherm controller in such a way that the controller could be control the fixed bed reactor temperature around the whole time of reduction period that was aspect according to reduction conditions.

The reduction procedure for catalyst is shown in Figure 10-2 and the reduction was started from room temperature at 16 ºC and the increasing in temperature was done by ramping. The whole reduction process was done at 1 bar pressure.

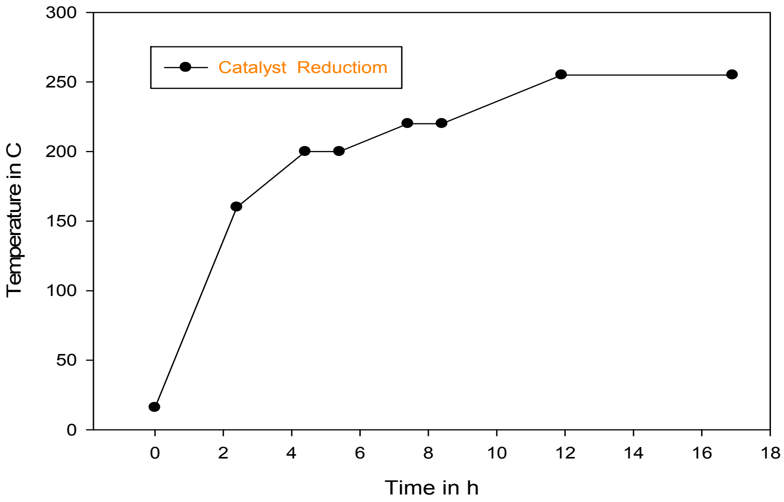


Figure 10-2Catalyst reduction before the reaction in Fixed Bed reactor

10.2 Methanol Experimental Setup

The experimental setup for methanol synthesis is designed by Hamidreza Bakhtiary and Xuyan Kim Phan as a part of their PhD work. This setup is build-up for conversion of synthesis gas into methanol and all the equipments are designed in such a way so that it can be worked at a pressure up to 100 bars and temperature up to 500 ºC. All parts in the rig are made of Stainless steel and the piping is mainly in ¼” with svagelok fitting. The Process diagram of methanol synthesis setup is shown in Figure-Appendix 1. There are three feed lines, one for Synthesis gas, one for hydrogen and other for nitrogen (other inert gas). The synthesis gas line is used for supply of feed gas into the reactor; H_2 and N_2 lines are used for leak test. All the three lines are used at high pressure around 80 bars. The lines are also equipped with manometers (a manometer is a device for measuring the pressure of fluid), manual valves, filters and ventilation valves. Bronkhorst digital mass flow meters are also be fitted in lines to control the feed gas flow and the pressure. The temperate in the reactor is controlled by digital Eurotherm controller which is connected with a furnace around the fixed bed reactor. The feed is preheated near the reaction temperature by heating band insulated around the feed line before the reactor.

10.2.1 Reactors

The laboratory scale fixed bed reactor (made of stainless steel with ½" in diameter) is connected with the setup and the tubular fixed bed is fitted with swagelokn VCR showing Figure 10-3. A thermo well is passed trough centre of the reactor and a movable thermocouple is used to measure of the temperature in the reactor. The catalyst bed temperature is measured by moving up and down the movable thermocouple along the reactor axis and the reactor is clumped with two parts of aluminium, so that heat from kanthal furnace is distributed uniformly around the whole reactor.

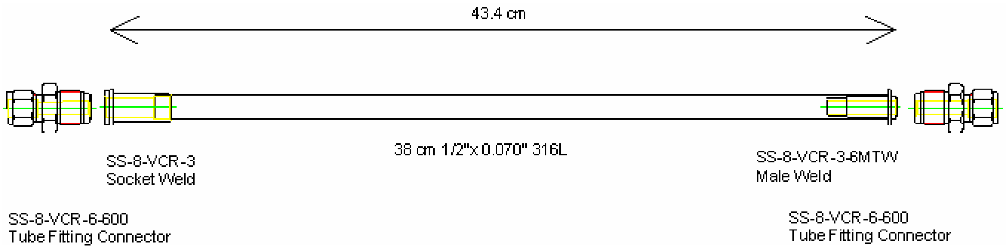


Figure 10-3 A fixed bed reactor configuration

10.2.2 Product analysis

A GC is used to analysis the product gas from the fixed bed reactor by allowing the product gas at atmospheric pressure through GC. GC calculates the percentage of H_2, N_2, CO, CO_2 and CH_4 in the product stream and also feed stream when it is analyzed The product is allowed to accumulate at the pressure of reaction in a container fitted with cooling water system bellow the reactor and it is allowed to pass in another container at atmospheric pressure where it is collected.

11 Health, Environment and safety

11.1 Set-up risk assessment

The risk assessment is the most important tools for a chemical process operation that we use for the systematic identification of issues linked to HES. 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.

So through risk assessment conducted prior to a concrete task or process, measures designed to eliminate or control the factors representing a potential risk can be implemented before the work starts. It also offers the possibility of increased control over factors/conditions that need to be checked during the actual carrying out of the task/process. The details descriptions and necessary data about HES are given in Appendix C.

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.

As described below activities is associated with several HES issues on the methanol synthesis set-up.

- Transport and mounting of the gas bottle
- Modification and maintained of experimental set-up
- Leak testing and reactor mounting
- Reaction experiment
- Experiment shut-down and dismounting of reactor
- Cleaning parts
- Handling of catalyst

For existing risk assessments, safety measures, rules and procedures are as in below-

- In the methanol synthesis set-up, a well established toxic and flammable gas alarm system is exist so for any incidence, the gas syncing 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 every one who is working in side the lab

11.2 Risk concerning with carbon monoxide

The carbon monoxide is colorless and odorless gas, it comes as synthesis gas component for methanol synthesis. The chemical company YARA PRAXAIR is supplier of synthesis gas in our lab. The carbon monoxide is extremely flammable and toxic gas. 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. Before use, special instruction should be read [44].

11.3 Risk concerning with methanol

The methanol is very dangerous poison and its vapor also harmful to human. It may cause 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. [44]

12 **Results and discussions**

12.1 Methanol synthesis catalyst

12.1.1 Catalyst characterization

The experiment was done on the Cu-based catalyst that was prepared by 2-steps co-precipitation followed ICI procedure.

12.1.1.1 X-Ray Diffraction

Figure 12-1 shows the XRD diffractograms for Cu-based catalyst in fresh (blue line in top), reduced (pink line in middle) and used (red line in bottom) form. In the fresh sample, ZnO is the main component present in crystal form and also small crystallites of CuO were detectable.

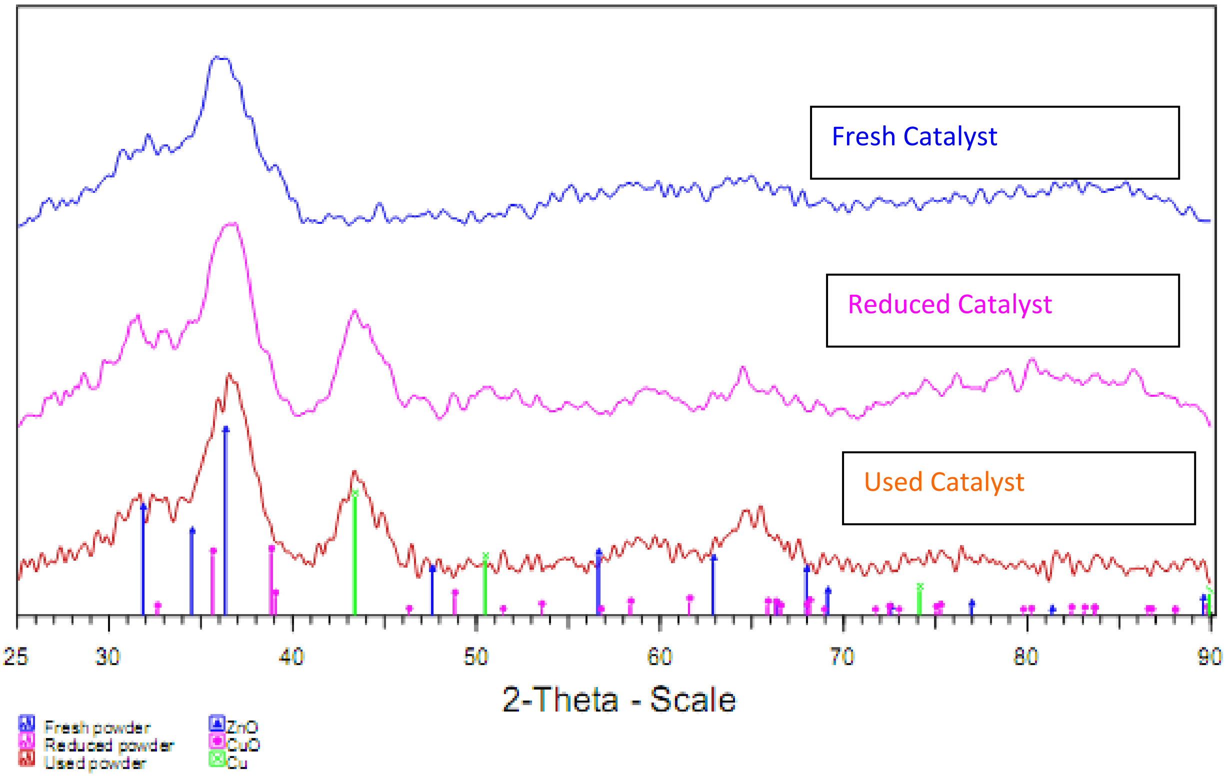


Figure 12-1 XRD for of $Cu/ZnO/Al_2O_3$ **which was produced by 2-steps co-precipitation followed ICI procedure.**

It should be noted that the broad peaks are the indication of the small crystallites and the no peak means vary small crystallites or amorphous phase. The reduction of CuO to Cu and possible of some sintering or agglomeration of Cu crystallites during 17 h of reduction period of time were also seen and during 240 h of reaction time, the Cu crystallites were not growth so much because the peaks were not sharpened.

12.1.1.2 Adsorption/Desorption

The BET surface area for $Cu/ZnO/Al_2O_3$ catalyst was measured by N_2 adsorption and desorption. The result is shown in Table 12.1

Table 12-1: BET result

Catalyst	$S_{BET}\ m^2/g$	**Pore width nm**
2nd batch $Cu/ZnO/Al_2O_3$	178	11.18282

In Table 12.1, the BET result showed that the prepared Cu-based catalyst has high surface area with porosity and possibly well mixed of $CuO-ZnO-Al_2O_3$. The ZnO and Al_2O_3 stabilize Cu and are structural promoters of the catalyst.

12.2 Experiments

The activity test of $Cu/ZnO/Al_2O_3$ were performed in the Fixed Bed Reactor and before the reaction started, the catalyst was reduced with synthesis gas around 17 h (as describe in sub-chapter-10.1.3)

12.2.1 Activity Test

The catalyst activity test was performed in fixed bed reactor abound 240 h and during this period, the conversion of CO and CO+ CO_2 were measured by product gas analysis from fixed bed reactor by continuous online GC operation. Conditions were as contact time 103 $ms.g_{cat}/cm^3$, pressure of 80 bars and temperature of 255°C. Synthesis gas compositions were $H_2/CO/CO_2/N_2$= 65/25/5/5 and the result is showing in Figure 12-2 and the result showed the almost constant conversion during 240 h reaction period of time.

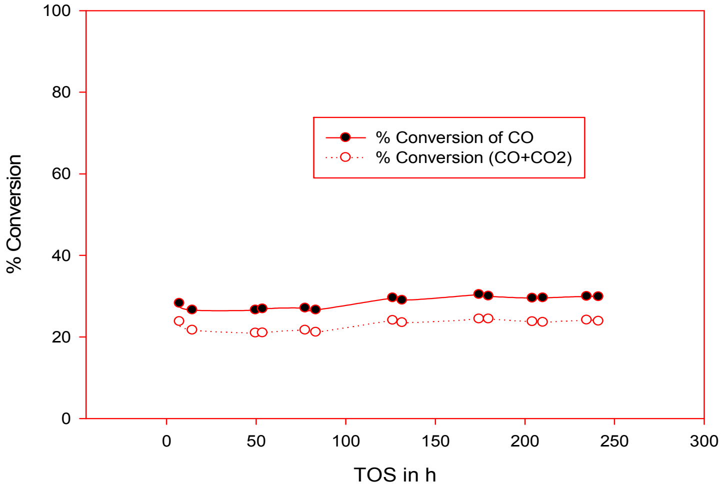


Figure12-2 Conversion of CO and CO+ CO_2 as a function of time on stream in fixed bed reactor when deactivation test is done by 2nd batch of Catalyst. Conditions: contact time 103 $ms.g_{cat}/cm^3$, pressure of 80 bars and temperature of 255°C. Synthesis gas compositions were $H_2/CO/CO_2/N_2$= 65/25/5/5

It should be mentioned that the details about the calibration of GC for both of gas phase and liquid phase are given in appendix (A1.1.3 and A 1.4) and all the mass balance are done based the equations (A1.1 and A 1.2) also given in the appendix.

Figure 12-1 shows the XRD diffractograms for Cu-based catalyst in fresh, reduced and used form. As mentioned, the fresh Cu-based catalyst power showed to be amorphous with peak of ZnO and CuO on overlapping. After reduction, the clear peak of ZnO and Cu were observed and used catalyst was similar with that of the reduced. This supports our conclusion that the deactivation of catalyst was negligible during the reaction time (240 h) [45].

As we seen in the Figure 12-2, the total conversion of $(CO + CO_2)$ was lower than the conversion of CO. According to Yang Y, et al. (2010) [48], WGS (water gas shift) reaction also occurs over the same catalyst and under the same conditions of methanol formation simultaneously and WGS reaction is faster than methanol formation. So because of faster WGS reaction, we experienced more CO_2 in the outlet of the fixed bed reactor compare to the inlet.

Coteron, A., et al, (1994), proposed a model for methanol synthesis from the synthesis gas and according to their experiments, methanol is produced by hydrogenation of CO_2 and the role of CO is the removal of oxygen adsorbed on the catalyst surface as a result of the reactions between CO_2 and H_2[46]. This is the consistent with our experimental observation for having more CO_2 in the outlet stream of the fixed reactor.

A comparison of activity between 1st batch and 2nd batch ICI catalysts are shown in Figure 12-3 as in below. Conditions were as contact time 103 $ms.g_{cat} / cm^3$, pressure of 80 bars and temperature of 255ºC. Synthesis gas compositions were $H_2 / CO / CO_2 / N_2$=65/25/5/5. The result exhibited that the 2nd batch was more active compare to the 1st batch catalyst and actually it is depend on the efficiency of catalyst making.

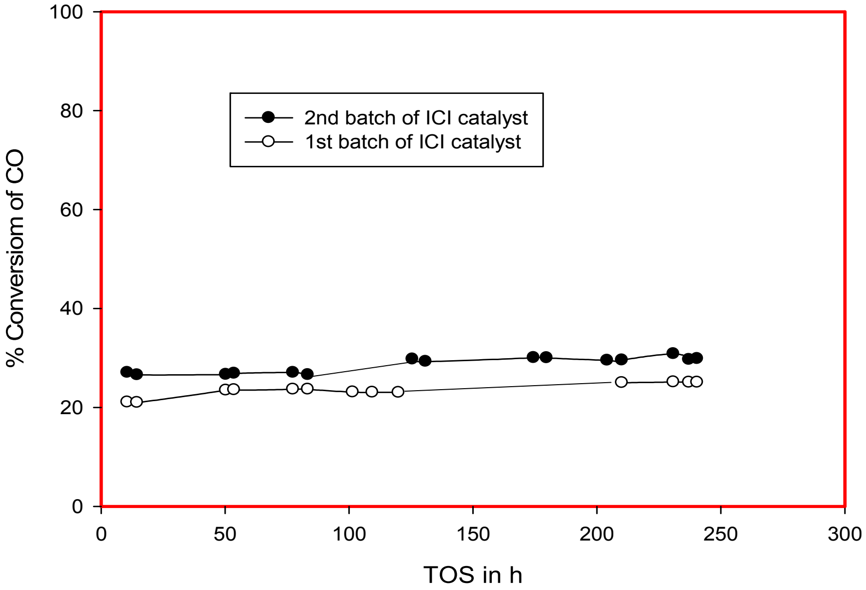


Figure 12-3 Conversion of CO as a function of time on stream in fixed bed reactor for 1st and 2nd batch of ICI catalysts. Conditions: contact time 103 $ms.g_{cat}/cm^3$, pressure of 80 bars and temperature of 255ºC. Synthesis gas compositions were $H_2/CO/CO_2/N_2$ = 65/25/5/5

[Note: the 1st catalyst was prepared by PhD student Xyun Kim Phan and that was used in my specialization project work and 2nd catalyst was prepared by me]

12.2.2 Kinetics of Methanol Synthesis

The kinetic study for methanol synthesis was carried out in this experimental thesis work and it has been observed that the apparent activation energy of methanol formation depends on the different feed gas compositions Figure 12-4 and Table 12.2.

The Figure-12.4 in below is shown lnk Vs 1000/T in K (Kelvin) at the conditions as pressure 80 bar and contact time 103 $ms.g_{cat}/cm^3$ for different feeds with different feed compositions. The Arrhenius diagrams for the pseudo-first order reaction shown in Figure 12-4 were done based on the materials balance, assumptions and equations that were mentioned in sub-chapter 7.2. The details about the feed compositions are given Table 12.2.

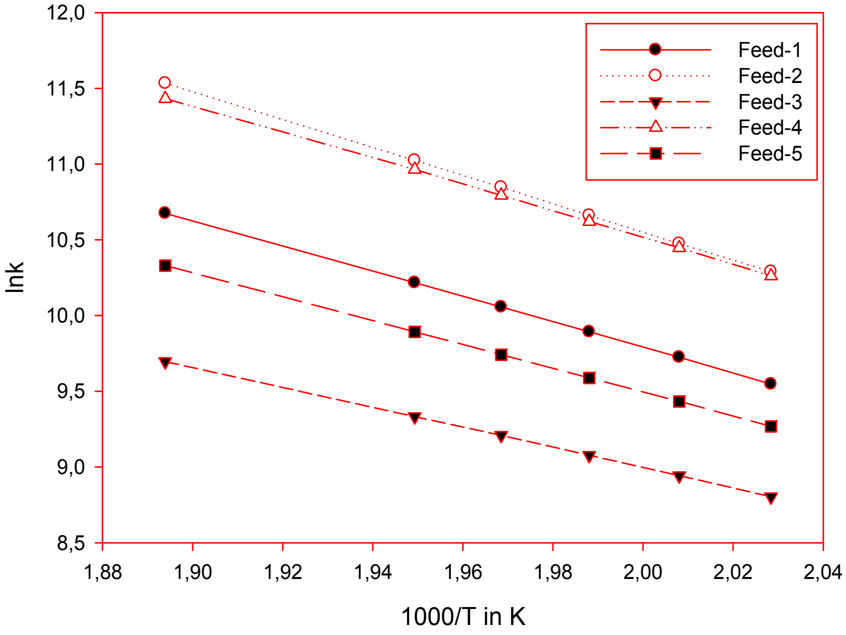


Figure 12-4 Arrhenius diagrams of the pseudo-first order reaction ($\ln k$ Vs $\frac{1000}{T}$) for different feeds. Conditions: Pressure=80 bar and Contact time 103 $ms.g_{cat}/cm^3$

The activation energy was calculated for different feeds according to the Arrhenius Equation (Equation 7.2.5) that was mentioned in sub-chapter 7.2 and the corresponding Arrhenius plots give apparent activation energy for methanol synthesis are shown in Table 12.2.

Table 12.2 shows, the activation energy of methanol synthesis for different feeds at the specific conditions of pressure and contact time and the partial pressure of corresponding feed.

Table 12-2: The activation energy of methanol synthesis for different feeds at the specific conditions of pressure and contact time and the partial pressure of corresponding feed

	P_{H_2} **bar**	P_{CO} **bar**	P_{CO2} **bar**	P_{N_2} **bar**	P_{CH_4} **bar**	E_a **KJ/mol**
Feed-1	44.8	22.4	4	4	4.8	**69.56**
Feed-2	33.6	33.6	4	4	4.8	**77.09**
Feed-3	53.76	13.44	4	4	4.8	**55.05**
Feed-4	22.4	22.4	4	26.4	4.8	**72.35**
Feed-5	52	20	4	4	0	**65.54**

According to Graaf, G. H., et al., (1990), the activation energy of methanol synthesis depends on the activity of catalyst and the activation energy increases with decreasing catalyst activity. They also found the different Arrhenius diagram for the different feed compositions on the same catalyst. So our experimental results are in consistent with Graaf, G. H., et al., (1990) [36]. A similar type of experiment was carried out on the activation energy of methanol synthesis by Dong, X., et al.,(2003). They found different activation energy for different the catalyst at the same conditions [47]

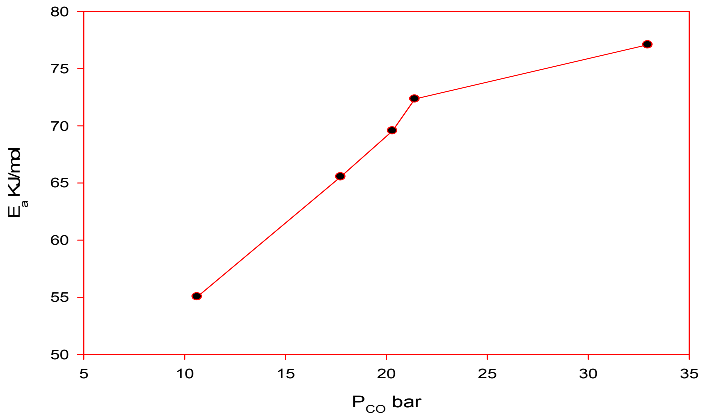


Figure 12-5 exhibited the apparent activation energy corresponding to the partial pressure of CO (P_{CO}) in feed gas and it was observed that the apparent activation energy was increased with increasing partial pressure of CO (P_{CO}) in feed gas. $E_a Vs P_{CO}$ Conditions: Pressure=80 bar, Temperature= 240°C and Contact time 103 $ms.g_{cat} / cm^3$.

Figure 12-5 exhibited the apparent activation energy corresponding to the partial pressure of CO (P_{CO}) in feed gas and it was observed that the apparent activation energy was increased with increasing partial pressure of CO (P_{CO}) in feed gas.

A similar trend was observed in Figure 12-6 and when the pressure fraction of $CO + CO_2$ was increased, the apparent activation energy also increased.

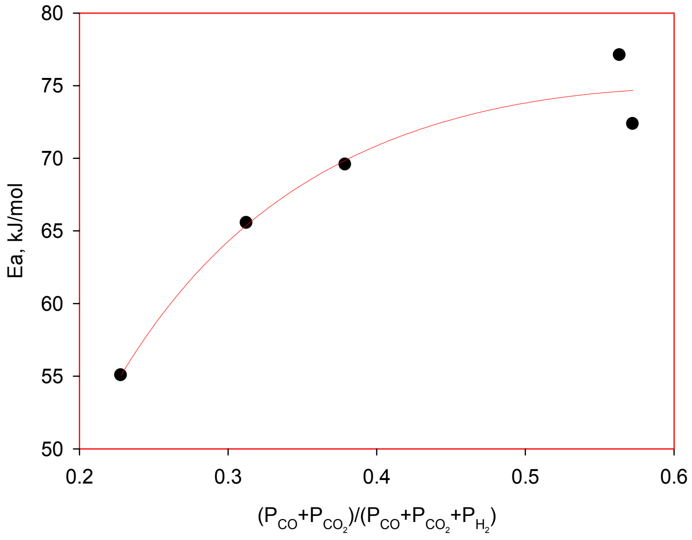


Figure 12-6 $E_a Vs \dfrac{P_{CO} + P_{CO_2}}{P_{CO} + P_{CO_2} + P_{H_2}}$**. Conditions: Pressure=80 bar, Temperature= 240°C and Contact time 103** $ms.g_{cat} / cm^3$**.**

From our experimental dates, we were tried to fine out a relationship between activation energy E_a and partial pressure of CO (P_{CO}) or the pressure fraction of ($CO + CO_2$) as shown in Figure 12-5 and Figure12-6 respectively. As seen in the mentioned figures, the activation energy E_a was increased with increasing of both P_{CO} and $\dfrac{P_{CO} + p_{CO_2}}{P_{CO} + p_{CO_2} + P_{H_2}}$.

According to Chorkendorff, I., et al., (2007), we found a relationship between activation energy, reaction order and partial pressure of reactant. As seen, when the partial pressure of a reactant is increased, the order of reaction corresponding to that reactant is decreased and activation energy is increased with respect to that particular reactant. Our results were shown similar trend as explained in the literature [39].

Table 12-3: productivity of methanol ($r_{CH_3OH} mol / g_{Cat.}$) with corresponding to the feed gas compositions.

	% of H_2	% of CO	% of CO_2	% of N_2	%of CH_4	$r_{CH_3OH} mol / g_{Cat.}$
Feed-1	56	28	5	5	6	3.587975
Feed-2	42	42	5	5	6	3.077836
Feed-3	67.2	16.8	5	5	6	3.225209
Feed-4	28	28	5	33	6	1.80249
Feed-5	65	25	5	5	0	3.427915

In Table 12.3 shown that the Feed-4 was exhibited minimum productivity of methanol formation due to highest inert content. According to Langmuir-Hinshelwood mechanism for multi-component reactant, when the partial pressure of one component is increased, the rate constant is also increased [49]. From Table 12.3, Feed-4 was contained 33% of N_2 where as other four feed were contained 5% N_2. As a result we observed lowest rate of methanol formation which was not similar with other four feeds. So for that cause, we did not use Feed-4 in the Figure 12-7 and Figure 12-8.

Figure 12-7 displayed the effect of $H_2 : CO$ ratio on the methanol productivity ($r_{CH_3OH} mol / g_{Cat.}$) at the conditions as pressure 80 bars, temperature 240 ºC and contact time 103 $ms.g_{cat} / cm^3$ for different feeds and the result shown that the productivity of methanol was increased up-to a point and then began to decrease with increasing $H_2 : CO$ ratio.

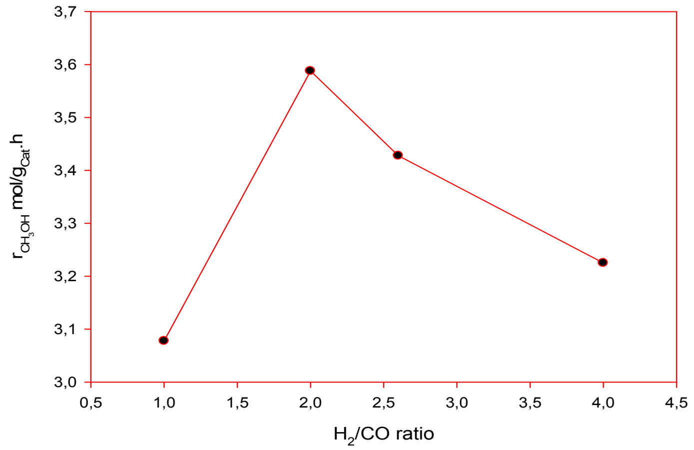


Figure 12-7 $r_{CH_3OH} mol / g_{Cat.} hVs \frac{H_2}{CO}$ **ratio. Conditions: Pressure=80 bar, Temperature= 240ºC and Contact time 103** $ms.g_{cat} / cm^3$

Figure 12-7showed, the maximum productivity of methanol was obtained when H_2/CO ratio was 2. According to the reference [47], we agreed that methanol is produced from hydrogenation of CO_2. If methanol is produced from CO_2 (according to reaction 7.1.1 which was described in sub-chapter 7.1), for maximum productivity of methanol the stoichiometric ratio of H_2/CO should be 3 and for CO the stoichiometric ratio of H_2/CO should be 2. Yang, Y., et al., (2010) [48] found that the faster RWGS (reverse water gas shift) reaction only leads to the accumulation of CO rather the methanol formation when methanol was produced from the mixture of CO_2 and H_2. According to reference [39] for maximum amount of methanol formation from a mixture of CO and, H_2 a minor amount of CO_2 is used. In practically, our experiment showed that the maximum productivity of methanol formation was at the ratio (H_2 to CO ratio) of 2 and the possible explanation was that the WGS reaction could be produced one mole of H_2 during the consumption of one mole of CO. So stoichiometrically need ratio 2 (H_2 to CO ratio) for maximum production of methanol.

A similar result was observed in Figure 12-7.

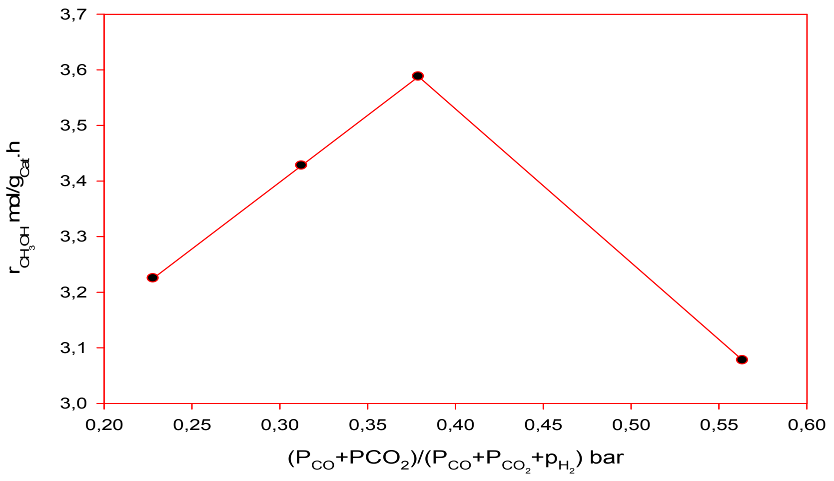


Figure 12-8 $r_{CH_3OH} mol/g_{Cat.}hVs\ \frac{P_{CO}+P_{CO_2}}{P_{CO}+P_{CO_2}+P_{H_2}}$**. At Pressure=80 bar, Temperature= 240°C and Contact time 103** $ms.g_{cat}/cm^3$**.**

12.2.3 The order of the methanol formation reaction

We have considered the Feed-3 and Feed-5, the partial pressure of P_{H_2} were assumed as constant and we were plotted $\ln r_{CO}$ Vs $\ln P_{CO}$. According to the power rate equation 7.3.3 shown in sub-chapter 7.3, the resulting slope of the curve exhibited the order of methanol formation with respect to CO.

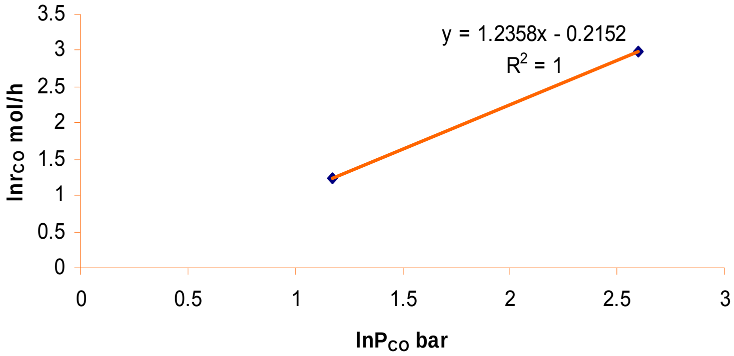


Figure12-9 : $\ln r_{CO}$ **Vs** $\ln P_{CO}$**. Conditions: assuming** P_{H_2} **constant in Feed-3 and Feed-5**

Also we have considered Feed-1 and Feed-5, the partial pressure of P_{CO} were assumed as constant and we were plotted $\ln r_{H_2}$ Vs $\ln P_{H_2}$. According to the power rate equation 7.3.3 shown in sub-chapter 7.3, the resulting slope of the curve exhibited the order of methanol formation with respect to H_2. Figure 12.10 and Figure 12.11 showed that the order of methanol formation with respect to CO was 1.23 and with respect to H_2 was 1.1.

It should be mentioned that the conditions for kinetics study were chosen in such a way that the % conversion of CO was between 10 to 20 because at the higher conversion it was possible to become at equilibrium conversion of CO and the equilibrium conversion could be affected the kinetics results.

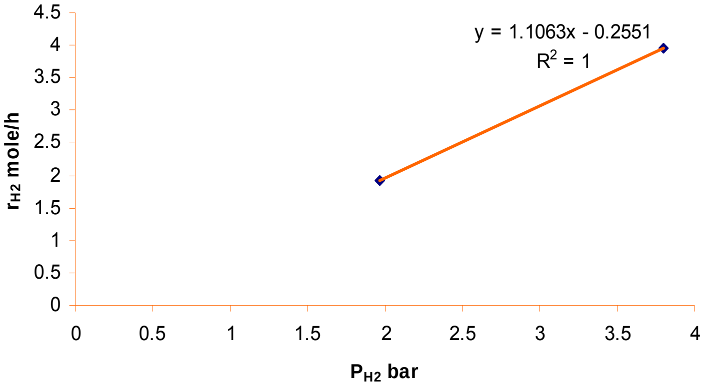


Figure12-10: $\ln r_{H_2}$ **Vs** $\ln P_{H_2}$ **. Conditions: assuming** P_{CO} **constant in Feed-1 and Feed-5**

13 Conclusions

A second batch of $Cu / ZnO / Al_2O_3$ for methanol synthesis was prepared following the method patented by ICI. The synthesized catalyst was characterized by using XRD and BET. The XRD results showed that the fresh catalyst was amorphous with peak of ZnO and CuO on overlapping and reduced catalyst clear peak with of ZnO and Cu and the used catalyst was similar with reduced catalyst. BET result exhibited the prepared catalyst has high surface area with porosity. It was concluded from XRD result and activity test report, the deactivation of synthesized ICI catalyst was not observed during 240 h of reaction period of time. The kinetics studies conformed us; (i) the activation energy of methanol formation was depended on the activity of catalyst as well as the compositions of the feed gas, (ii) the activation energy was increased with the increasing of the partial pressure of CO and as well as the pressure fraction of $(CO + CO_2)$, (iii) the maximum productivity of methanol was obtained when the ratio of H_2 / CO was 2, and (iv) the order of the methanol formation reaction was 1.1 and 1.23 respectively with H_2 and CO. Besides that, our finding with many other literatures supported that methanol is produced by hydrogenation of CO_2 and the role of CO is the removal of oxygen adsorbed on the catalyst surface as a result of the reactions between CO_2 and H_2.

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Appendices

Appendix A: Process Diagram of the Methanol Synthesis Experimental Setup

Appendix **A**.1: Methanol Experimental Setup

Appendix **A**.1.1: Reactors

Appendix A.1.2: Product analysis

Appendix A.1.3: Gas Chromatograph Analyses

Appendix A.1.3.1: the calibration of GC for gas phase analysis

Appendix A.1.4: the calibration of GC for liquid phase analysis

Appendix A.1.5: Calibration Curve for Mass flow Controller at Methanol Synthesis Experimental Setup

Appendix B: Data form the GC Analysis for activation test of catalyst

Appendix C: Health, Environment and safety

Appendix D: Hazardous activity identification process in methanol synthesis rig.

Appendix E: the existing risk assessment analysis data sheet of methanol synthesis experimental set-up

Appendix F: The materials, safety and data sheets for all the gas and chemical are given in bellow

Appendix G: Regarding to the HES I did the following courses and training

Appendix A

Process Diagram of the Methanol Synthesis Experimental Setup

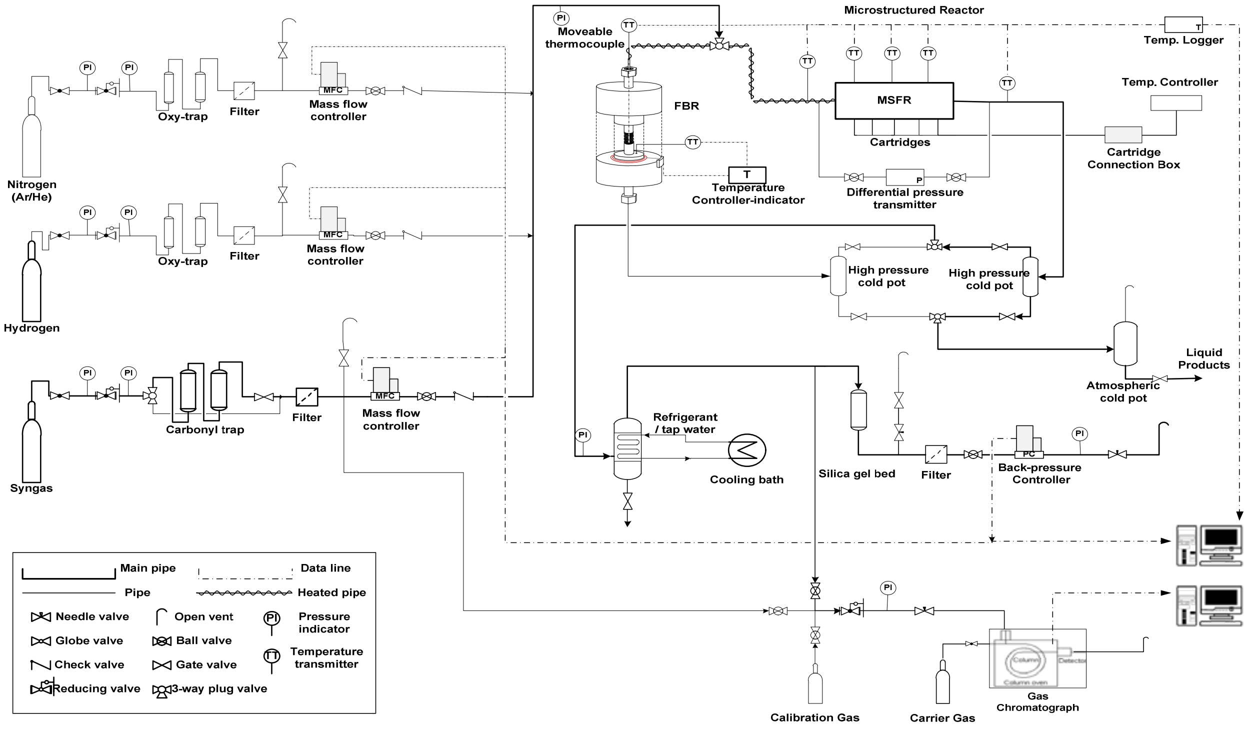


Figure A- 1:Process Diagram of the Methanol Synthesis Experimental Setup

Appendix A.1: Methanol Experimental Setup

The experimental setup for methanol synthesis is designed by Hamidreza Bakhtiary and Xuyan Kim Phan as a part of their PhD work. This setup is build-up for conversion of synthesis gas into methanol and all the equipments are designed in such a way so that it can be worked at a pressure up to 100 bars and temperature up to 500 ºC. All parts in the rig is made of Stainless steel and the piping is mainly in ¼" with svagelok fitting. The Process diagram of methanol synthesis setup is shown in Figure-Appendix1. There are three feed lines, one for Syngas, one for hydrogen and other for nitrogen (other inert gas). The syngas line is used for supply of feed gas into the reactor; H_2 and N_2 lines are used for leak test. All the three lines are used at high pressure around 80 bars. The lines are also equipped with manometers (a manometer is a device for measuring the pressure of fluid), manual valves, filters and ventilation valves. Bronkhorst digital mass flow meters are also be fitted in lines to control the feed gas flow and the pressure. The temperate in the reactor is controlled by digital Eurotherm controller which is connected with a furnace around the fixed bed reactor. The feed is preheated near the reaction temperature by heating band insulated around the feed line before the reactor.

Appendix A.1.1: Reactors

The laboratory scale fixed bed reactor (made of stainless steel with ½" in diameter) is connected with the setup and the tubular fixed bed is fitted with swagelokn VCR showing Figure 10-3. A thermo well is passed trough centre of the reactor and a movable thermocouple is used to measure of the temperature in the reactor. The catalyst bed temperature is measured by moving up and down the movable thermocouple along the reactor axis and the reactor is clumped with two parts of aluminium, so that heat from kanthal furnace is distributed uniformly around the whole reactor.

Appendix A.1.2: Product analysis

A GC is used to analysis the product gas from the fixed bed reactor by allowing the product gas at atmospheric pressure through GC. GC calculates the percentage of H_2, N_2, CO, CO_2 and CH_4 in the product stream and also feed stream when it is analyzed The product is allowed to accumulate at the pressure of reaction in a container fitted with cooling water system bellow the reactor and it is allowed to pass in another container at atmospheric pressure where it is collected.

The following formulas are used to measure the % conversion of CO and CO_2 as in bellow.

% Conversion of CO:

$$X_{CO} = \frac{n_{COin} - n_{COout}}{n_{COin}} * 100 \ldots\ldots\ldots\ldots\ldots\ldots \text{(A 1.1)}$$

% Conversion of CO_2:

$$X_{CO_2} = \frac{n_{CO_2in} - n_{CO_2out}}{n_{CO_2in}} * 100 \ldots\ldots\ldots\ldots\ldots\ldots \text{(A 1.2)}$$

The contact time (ms):

$$W / F = \frac{m_{cat}}{F(\frac{cm^3_{Syngas}}{ms})} \ldots\ldots\ldots\ldots\ldots\ldots \text{(A 1.3)}$$

Here X_{CO} and X_{CO_2} are the Conversion of CO and CO_2 respectively. CO in feed gas and product gas are shown as n_{COin} and n_{COout}. CO_2 in feed and product gas are shown as n_{CO_2in} and n_{CO_2out} respectively. W is the weight of catalyst and F is the feed gas flow rate.

Appendix A.1.3: Gas Chromatograph Analyses

The Gas Chromatograph (GC) is an Agilent 6890N with TCD and FID detectors installed. The system is capable to do online feed and product gas analysis as well as offline liquid product analysis. A selection valve is installed to chose between gas and liquid analyses.

Appendix A.1.3.1: the calibration of GC for gas phase analysis

The calibration of gas phase analysis was done by SINTEF Research Scientist Rune Myrstad in December 2005. The calibration curve for each component identify by TCD detector are shown in below.

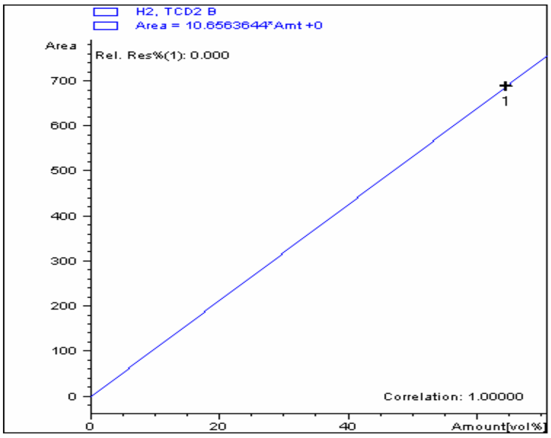


Figure A- 2:**Calibration Curve for** H_2

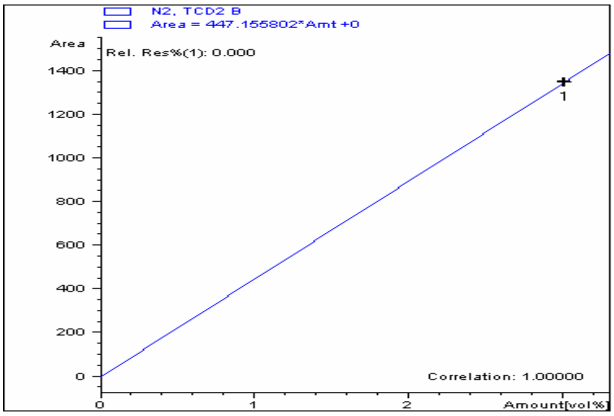


Figure A- 3: **Calibration Curve for** N_2

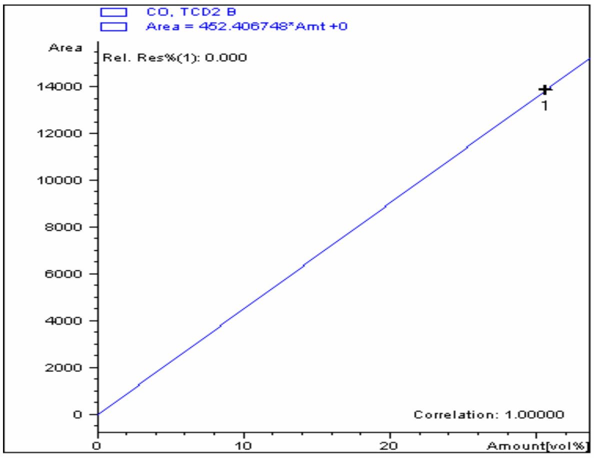


Figure A- 4: **Calibration Curve for CO**

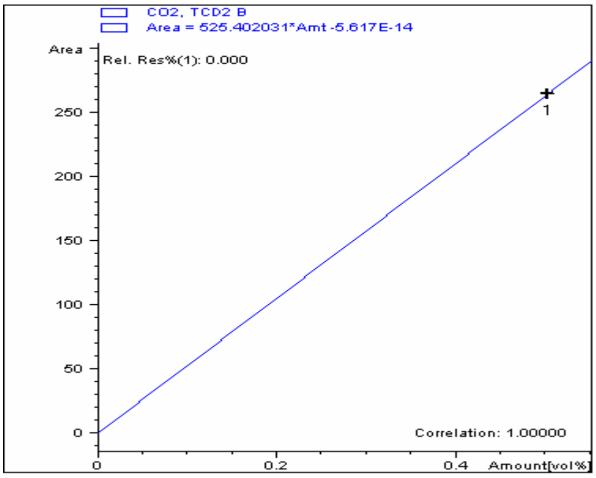


Figure A- 5: **Calibration Curve for** CO_2

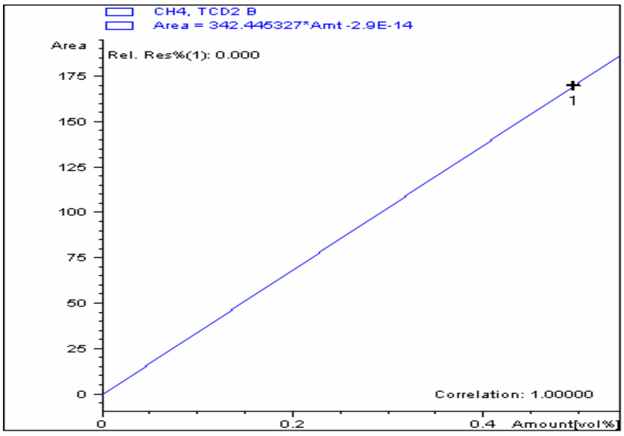


Figure A- 6: **Calibration Curve for** CH_4

Appendix A.1.4: the calibration of GC for liquid phase analysis

The calibration of liquid phase analysis was done together with PhD student Xuyen Kim Phan and Hamidreza Bakthiary in February 2008. The GC software calculated the calibration curves for each compound identify by FID detector are given in below.

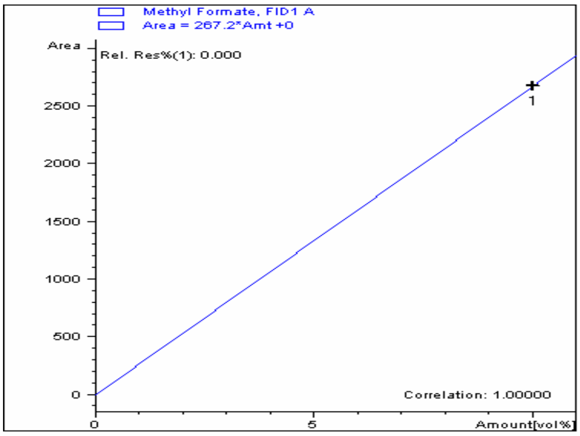


Figure A- 7: **Calibration Curve for Methylformate**

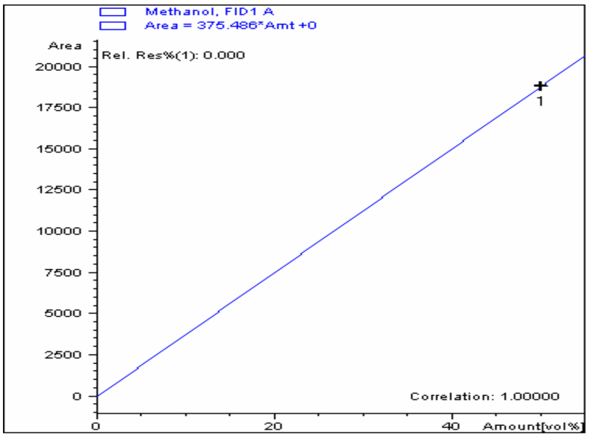


Figure A- 8: **Calibration Curve for Methanol**

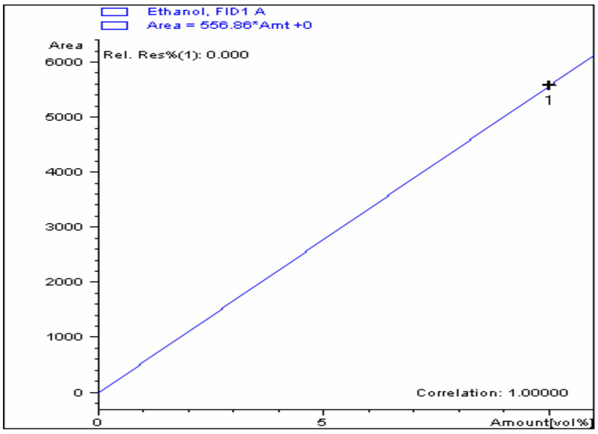


Figure A- 9: **Calibration Curve for Ethanol**

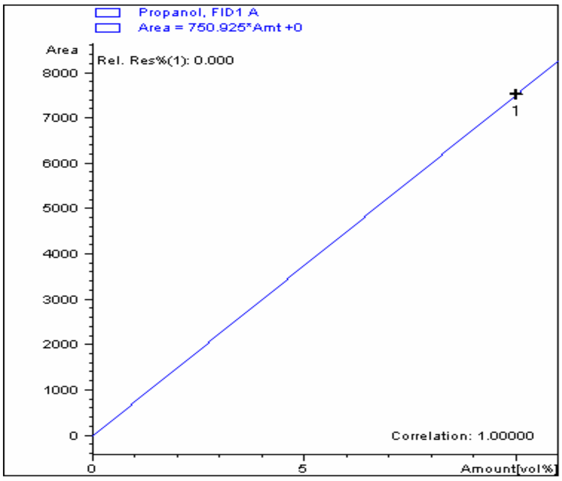


Figure A- 10: **Calibration Curve for Propanol**

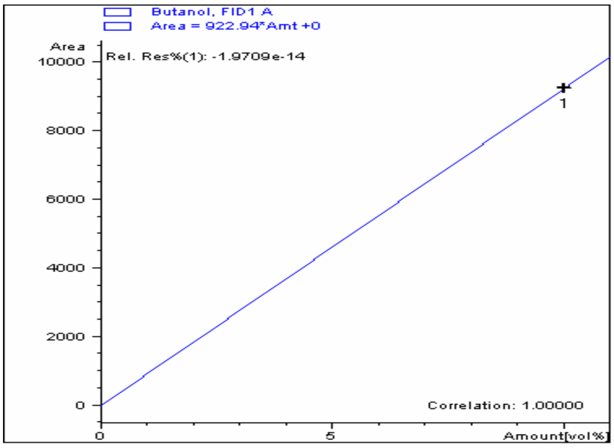


Figure A- 11: **Calibration Curve for Butanol**

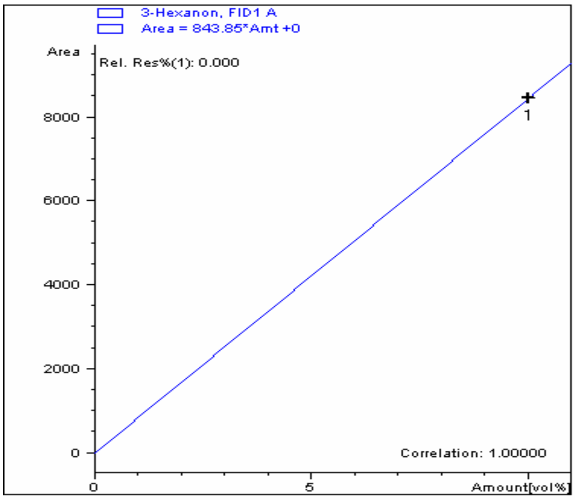


Figure A- 12: **Calibration Curve for 3-Hexanon**

Appendix A.1.5: Calibration Curve for Mass flow Controller at Methanol Synthesis Experimental Setup

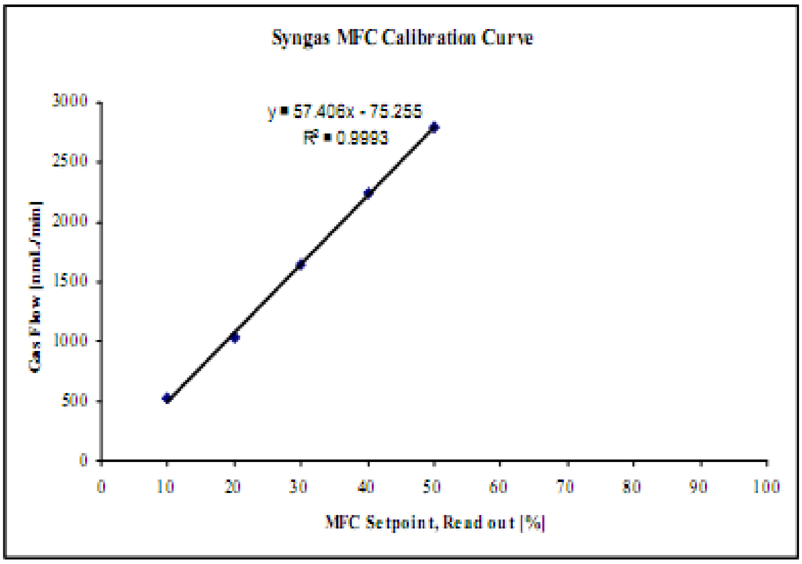


Figure A- 13: **Calibration Curve for Synthesis Gas.**

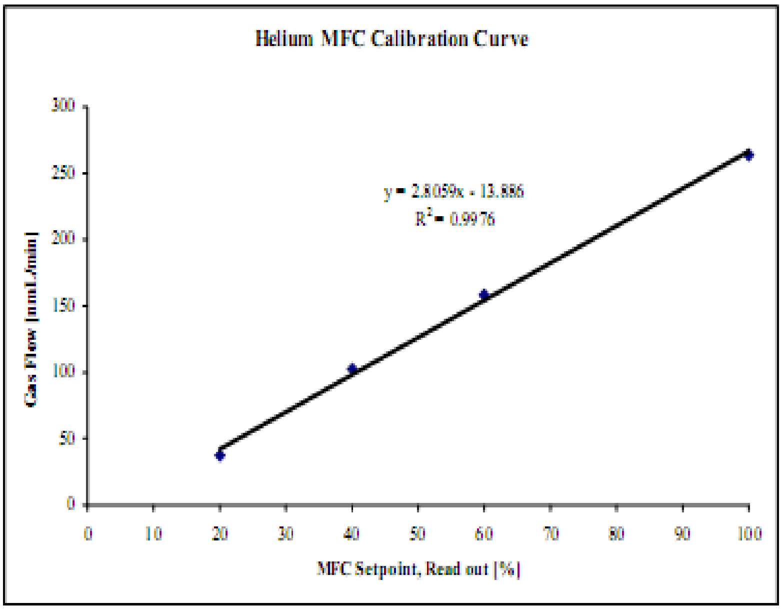


Figure A- 14: **Calibration Curve for Helium Gas**

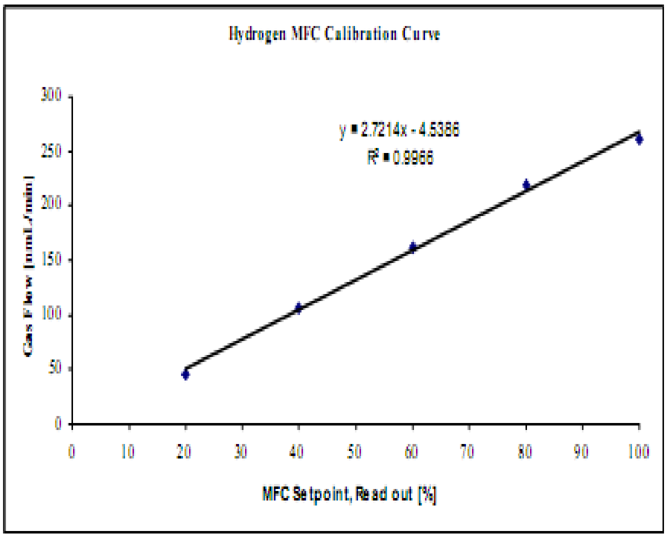


Figure A- 15: **Calibration Curve for Hydrogen Gas**

Appendix B

Data form the GC Analysis for activation test of catalyst

Table B- 1: **Data from the GC Analysis of the Feedstock Gas and calculation of the Area Ratios.**

Analysis No	Comments	AN_2	ACO	ACO_2	ACO/AN_2	ACO_2/AN_2	ACO/ACO_2
8	001F0108	1893.32	9197.88	1171.99	4.858069423	0.619013162	7.848087441
16	001F0116	1885.56	8941.8	1120.39	4.742251639	0.594194828	7.980970912
24	001F0124	1887.44	8983.02	1665.28	4.759367185	0.882295596	5.394300058
32	001F0132	1888.35	9036.4	1280.12	4.7853417	0.67790399	7.059025716
33	001F0133	1880.81	8999.19	1291.55	4.78474168	0.686698816	6.967744183
34	001F0134	1881.79	9006.75	1307.46	4.786267331	0.694795912	6.88873847
35	001F0135	1883.52	9015.4	1323.72	4.786463643	0.70279052	6.810654821
36	001F0136	1880.88	9004.3	1338.63	4.787280422	0.711704096	6.726503963
37	001F0137	1881.07	8999.4	1354.79	4.784191976	0.720223065	6.642653105
38	001F0138	1862.1	8908.9	1360.39	4.78432952	0.730567639	6.548783805
39	001F0139	1878	8985.78	1392.23	4.784760383	0.741336528	6.454235292
				AVERAGE	4.784	0.883	

Table B- 2: **Calculation of CO and CO+CO₂% Conversion for Cu-based catalyst in FBR. Conditions: pressure 80 bars, temperature 255 ºC, contact time 103** $ms.g_{cat}/cm^3$

Analysis No	Comments	ACO/AN_2	ACO_2/AN_2	CO% Conv.	$CO+CO_2$% Conv.	TOS(h)
2	001F0102	3.48	0.41	27.20	31.20	1.98
3	001F0103	3.48	0.42	27.30	31.19	2.64
4	001F0104	3.46	0.44	27.80	31.15	3.3
5	001F0105	3.42	0.50	28.45	30.65	3.96
6	001F0106	3.39	0.59	29.048	29.61	4.62
7	001F0107	3.38	0.68	29.42	28.30	5.28
8	001F0108	3.37	0.76	29.58	26.97	5.94
9	001F0109	3.38	0.83	29.28	25.53	6.6
10	001F0110	3.43	0.88	28.24	23.76	7.26
11	001F0111	3.46	0.90	27.69	22.91	7.92
12	001F0112	3.47	0.91	27.37	22.46	8.58
13	001F0113	3.48	0.92	27.19	22.346	9.24
14	001F0114	3.49	0.91	27.04	22.29	9.9
15	001F0115	3.49	0.91	26.94	22.24	10.56
16	001F0116	3.50	0.91	26.80	22.12	11.22

17	001F0117	3.50	0.91	26.72	22.04	11.88
18	001F0118	3.501	0.91	26.69	21.97	12.54
19	001F0119	3.51	0.92	26.69	21.90	13.2
20	001F0120	3.51	0.92	26.64	21.78	13.86
21	001F0121	3.51	0.93	26.58	21.66	14.52
New sequence: 2	001F0102	4.401383072	0.968581385	7.997845475	5.241495361	45.12
3	001F0103	3.911324631	0.965125264	18.241542	13.95006362	45.78
4	001F0104	3.676103023	0.961412147	23.15838163	18.16631074	46.44
5	001F0105	3.588685576	0.961747621	24.9856694	19.70296107	47.1
6	001F0106	3.548209142	0.96231397	25.8317487	20.40721524	47.76
7	001F0107	3.527783571	0.963969677	26.25870462	20.73842864	48.42
8	001F0108	3.518899584	0.965803386	26.4444067	20.86283801	49.08
9	001F0109	3.512437685	0.968472014	26.57947984	20.92977415	49.74
10	001F0110	3.508599301	0.971310261	26.65971362	20.9474226	50.4
11	001F0111	3.505376754	0.973708944	26.72707454	20.96196051	51.06
12	001F0112	3.502815146	0.976393318	26.78061985	20.95979417	51.72
13	001F0113	3.500453956	0.977813156	26.82997583	20.97640529	52.38
14	001F0114	3.500758796	0.978914351	26.82360376	20.95159437	53.04
15	001F0115	3.498179655	0.980168155	26.87751557	20.97498129	53.7
New sequence: 2	001F0102	4.401383072	0.968581385	7.997845475	5.241495361	45.12
3	001F0103	3.911324631	0.965125264	18.241542	13.95006362	45.78
4	001F0104	3.676103023	0.961412147	23.15838163	18.16631074	46.44
5	001F0105	3.588685576	0.961747621	24.9856694	19.70296107	47.1
6	001F0106	3.548209142	0.96231397	25.8317487	20.40721524	47.76
7	001F0107	3.527783571	0.963969677	26.25870462	20.73842864	48.42
8	001F0108	3.518899584	0.965803386	26.4444067	20.86283801	49.08
9	001F0109	3.512437685	0.968472014	26.57947984	20.92977415	49.74
10	001F0110	3.508599301	0.971310261	26.65971362	20.9474226	50.4
11	001F0111	3.505376754	0.973708944	26.72707454	20.96196051	51.06
12	001F0112	3.502815146	0.976393318	26.78061985	20.95979417	51.72
13	001F0113	3.500453956	0.977813156	26.82997583	20.97640529	52.38
14	001F0114	3.500758796	0.978914351	26.82360376	20.95159437	53.04
15	001F0115	3.498179655	0.980168155	26.87751557	20.97498129	53.7

Analysis No	**Comments**	**ACO/AN_2**	**ACO_2/AN_2**	**CO% Conv.**	**$CO+CO_2$% Conv.**	**TOS(h)**
New sequence: 2	001F0102	3.812912624	0.94636492	20.29864916	16.01768934	74.16
3	001F0103	3.680448527	0.94706503	23.06754752	18.34279942	74.82
4	001F0104	3.604674979	0.947553701	24.65144275	19.67127793	75.48
5	001F0105	3.565459586	0.947702597	25.47116249	20.36064614	76.14
6	001F0106	3.542509558	0.948315762	25.95088716	20.75480288	76.8
7	001F0107	3.490173868	0.949949259	27.04486062	21.64949485	77.46
8	001F0108	3.525948939	0.950708577	26.29705396	21.00480826	78.12
9	001F0109	3.521951466	0.951057856	26.38061318	21.06918437	78.78
10	001F0110	3.518274156	0.993057628	26.45748001	20.3929454	79.44
11	001F0111	3.514850605	0.951225704	26.52904253	21.19152445	80.1
12	001F0112	3.514685873	0.952263565	26.53248594	21.17611722	80.76
13	001F0113	3.513242889	0.953239861	26.56264865	21.1843524	81.42
15	001F0115	3.511539253	0.95697918	26.59825977	21.14843069	82.74
New sequence: 2	001F0102	1.871035741	0.939240006	60.88972113	50.40981564	123
3	001F0103	2.877160058	0.940163947	39.85869443	32.63942112	123.66
4	001F0104	3.245643613	0.929747956	32.15627899	26.32095342	124.32
5	001F0105	3.341800131	0.928400611	30.14631833	24.6479488	124.98

6	001F0106	3.360454604	0.930030178	29.7563837	24.29001621	125.64
7	001F0107	3.369453805	0.934621339	29.56827331	24.05020038	126.3
8	001F0108	3.376121878	0.937286765	29.42889051	23.88550126	126.96
9	001F0109	3.373747721	0.939305247	29.47851753	23.89177752	127.62
10	001F0110	3.369377274	0.938993755	29.56987304	23.97439512	128.28
11	001F0111	3.368298571	0.939651424	29.59242117	23.98182468	128.94
12	001F0112	3.369308614	0.938453391	29.57130823	23.98514195	129.6
13	001F0113	3.375482542	0.936976859	29.44225456	23.90225163	130.26
14	001F0114	3.38302431	0.937579259	29.2846089	23.75853946	130.92
15	001F0115	3.396449753	0.939284793	29.00397673	23.49153791	131.58
New sequence: 2	001F0102	1.515681736	0.825368918	68.31768946	58.6897714	171.84
3	001F0103	2.518369091	0.897939995	47.35850562	39.71573873	172.5
4	001F0104	3.065452936	0.934512113	35.92280653	29.41653347	173.16
5	001F0105	3.272364344	0.948612877	31.59773529	25.51654808	173.82
6	001F0106	3.329294592	0.954860482	30.40772174	24.40171035	174.48
8	001F0108	3.34339448	0.959497824	30.11299164	24.07107281	175.8
10	001F0110	3.345431397	0.957567215	30.07041395	24.06919691	177.12
12	001F0112	3.345784092	0.953372602	30.06304155	24.13699145	178.44
13	001F0113	3.347945952	0.95189887	30.01785218	24.12484874	179.1
New sequence: 2	001F0102	1.257206477	0.731527943	73.7206004	64.90675102	201.54
3	001F0103	2.224754696	0.831117034	53.49593028	46.07602384	202.2
4	001F0104	2.912100772	0.89888608	39.12832835	32.75124666	202.86
5	001F0105	3.234689711	0.932848394	32.38524851	26.45953583	203.52
6	001F0106	3.37224765	0.950993053	29.50987353	23.71200454	204.18
7	001F0107	3.376690623	0.958605111	29.41700203	23.49928122	204.84
10	001F0110	3.360010465	0.961382338	29.76566754	23.74461262	206.82
12	001F0112	3.36312531	0.960566912	29.7005579	23.70403702	208.14
13	001F0113	3.368371811	0.960733543	29.59089025	23.60851679	208.8
14	001F0114	3.369899699	0.960409256	29.55895279	23.58727802	209.46
New sequence: 2	001F0102	1.733527747	0.807471295	63.76405211	55.16147799	231.9
3	001F0103	2.688801361	0.886185646	43.79595818	36.91570485	232.56
4	001F0104	3.151897636	0.925951775	34.11585209	28.04218437	233.22
5	001F0105	3.308736366	0.94151672	30.83745054	24.99994554	233.88

Analysis No	**Comments**	**ACO/AN_2**	**ACO_2/AN_2**	**CO% Conv.**	**$CO+CO_2$% Conv.**	**TOS(h)**
6	001F0106	3.351405465	0.94953619	29.94553794	24.10549399	234.54
7	001F0107	3.359903382	0.955332654	29.7679059	23.85325506	235.2
10	001F0110	3.363326638	0.961240953	29.69634953	23.68859023	237.18
12	001F0112	3.361211154	0.961703825	29.74056951	23.71775227	238.5
14	001F0114	3.353718583	0.959282043	29.89718681	23.89270114	239.82
15	001F0115	3.355480746	0.958317035	29.8603523	23.87863453	240.48

Table B- 3: **the value of rate constant corresponding to the feed gas**

Temperature ºC	Feed-1	Feed-2	Feed-3	Feed-4	Feed-5
255	43232.68	102065.4	16245.6	92179.25	30642.97
240	27371.25	61283.99	11291.42	57761.78	19785.65
235	23310.76	51369.93	9980.321	48703.96	17001.19
230	19773.72	42639.07	8753.383	40966.23	14588.21
225	16728.45	35399.83	7654.688	34414.22	12492.58
220	14012.63	29410.9	6659.027	28603.97	10597.95

Appendix C

Health, Environment and safety

Appendix C.1: Set-up risk assessment

The rick assessment is the most important tools for a chemical process operation that we use for the systematic identification of issues linked to HES. A rick assessment must be carried out prior to the commencement of a specified chemical process and again when the process is modified. This rick assessment is done to remove or control the rick factors during the operational period of the chemical process.

So through risk assessment conducted prior to a concrete task or process, measures designed to eliminate or control the factors representing a potential risk can be implemented before the work starts. It also offers the possibility of increased control over factors/conditions that need to be checked during the actual carrying out of the task/process. The details descriptions and necessary data about HES are given in Appendix C.

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.

As described below activities is associated with several HES issues on the methanol synthesis set-up.

- Transport and mounting of the gas bottle
- Modification and maintained of experimental set-up
- Leak testing and reactor mounting
- Reaction experiment
- Experiment shut-down and dismounting of reactor
- Cleaning parts

- Handling of catalyst

For existing risk assessments, safety measures, rules and procedures are as in below-

- In the methanol synthesis set-up, a well established toxic and flammable gas alarm system is exist so for any incidence, the gas syncing 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 every one who is working in side the lab

Appendix C.2: Risk concerning with carbon monoxide

The carbon monoxide is colorless and odorless gas, it comes as synthesis gas component for methanol synthesis. The chemical company YARA PRAXAIR is supplier of synthesis gas in our lab. The carbon monoxide is extremely flammable and toxic gas. 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. Before use, special instruction should be read [44].

Appendix C.3: Risk concerning with methanol

The methanol is very dangerous poison and its vapor also harmful to human. It may cause 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. [44]

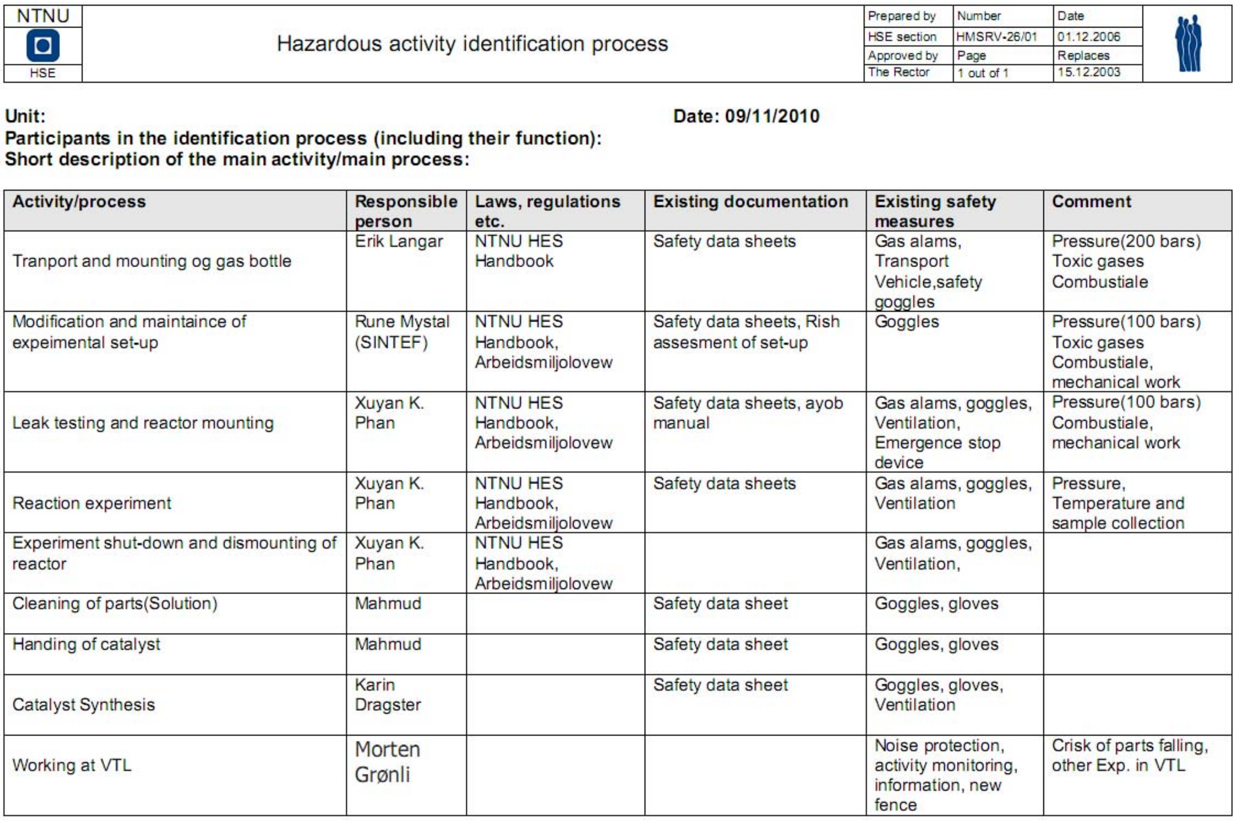
Appendix C.4: Risk concerning with Hydrogen

The Hydrogen is 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 any one 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 [44]

Appendix D

Hazardous activity identification process in methanol synthesis rig.

Table D- 1: Hazardous activity identification process in methanol synthesis rig.



NTNU	Hazardous activity identification process	Prepared by	Number	Date
HSE		HSE section	HMSRV-26/01	01.12.2006
		Approved by	Page	Replaces
		The Rector	1 out of 1	15.12.2003

Unit: **Date: 09/11/2010**

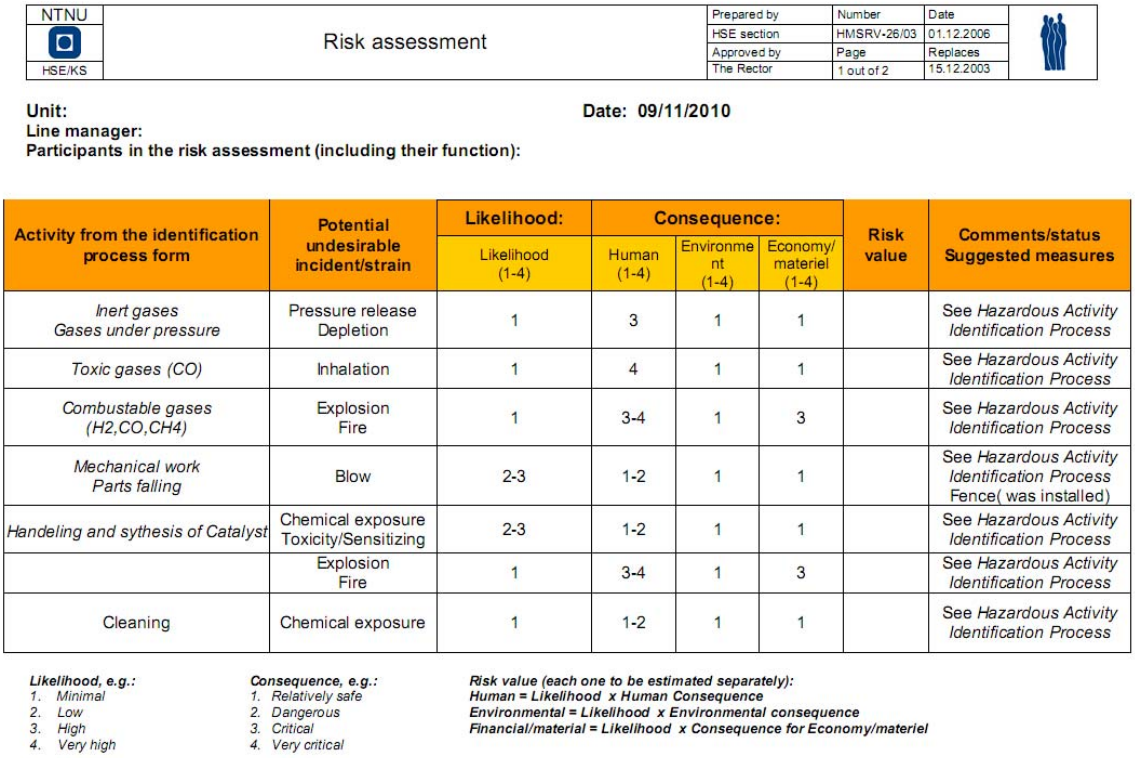
Participants in the identification process (including their function):

Short description of the main activity/main process:

Activity/process	Responsible person	Laws, regulations etc.	Existing documentation	Existing safety measures	Comment
Tranport and mounting og gas bottle	Erik Langar	NTNU HES Handbook	Safety data sheets	Gas alams, Transport Vehicle,safety goggles	Pressure(200 bars) Toxic gases Combustiale
Modification and maintaince of expeimental set-up	Rune Mystal (SINTEF)	NTNU HES Handbook, Arbeidsmiljolovew	Safety data sheets, Rish assesment of set-up	Goggles	Pressure(100 bars) Toxic gases Combustiale, mechanical work
Leak testing and reactor mounting	Xuyan K. Phan	NTNU HES Handbook, Arbeidsmiljolovew	Safety data sheets, ayob manual	Gas alams, goggles, Ventilation, Emergence stop device	Pressure(100 bars) Combustiale, mechanical work
Reaction experiment	Xuyan K. Phan	NTNU HES Handbook, Arbeidsmiljolovew	Safety data sheets	Gas alams, goggles, Ventilation	Pressure, Temperature and sample collection
Experiment shut-down and dismounting of reactor	Xuyan K. Phan	NTNU HES Handbook, Arbeidsmiljolovew		Gas alams, goggles, Ventilation,	
Cleaning of parts(Solution)	Mahmud		Safety data sheet	Goggles, gloves	
Handing of catalyst	Mahmud		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	Crisk of parts falling, other Exp. in VTL

Appendix D.1: The risk assessments for methanol synthesis rig

Table D- 2: **The risk assessments for methanol synthesis rig**



NTNU HSE/KS	Risk assessment	Prepared by HSE section	Number HMSRV-26/03	Date 01.12.2006
		Approved by The Rector	Page 1 out of 2	Replaces 15.12.2003

Unit: **Date: 09/11/2010**
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 (H2,CO,CH4)	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*
	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*

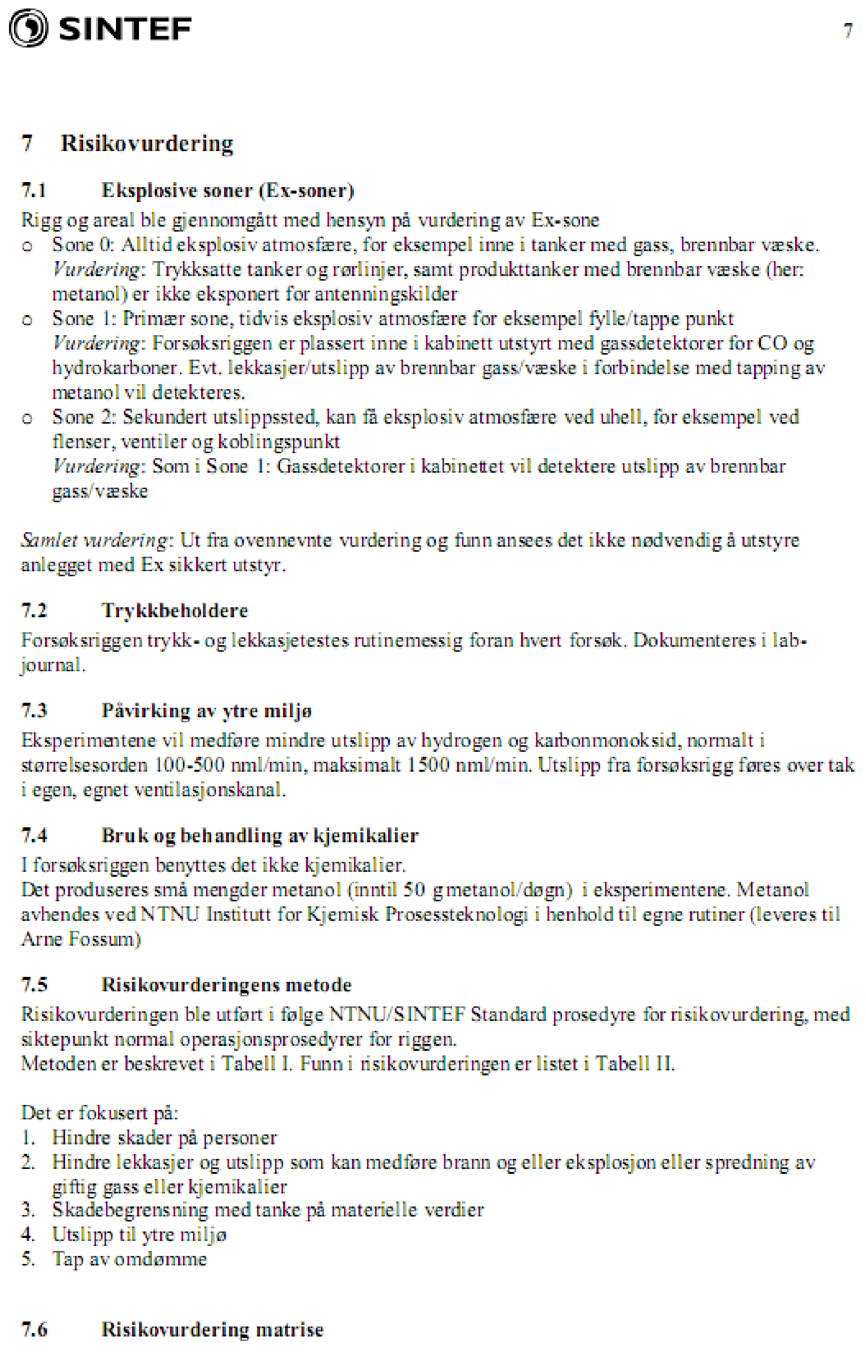
Likelihood, e.g.:
1. *Minimal*
2. *Low*
3. *High*
4. *Very high*

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

Appendix E

The existing risk assessment analysis data sheet of methanol synthesis experimental set-up.



SINTEF

7

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.

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)

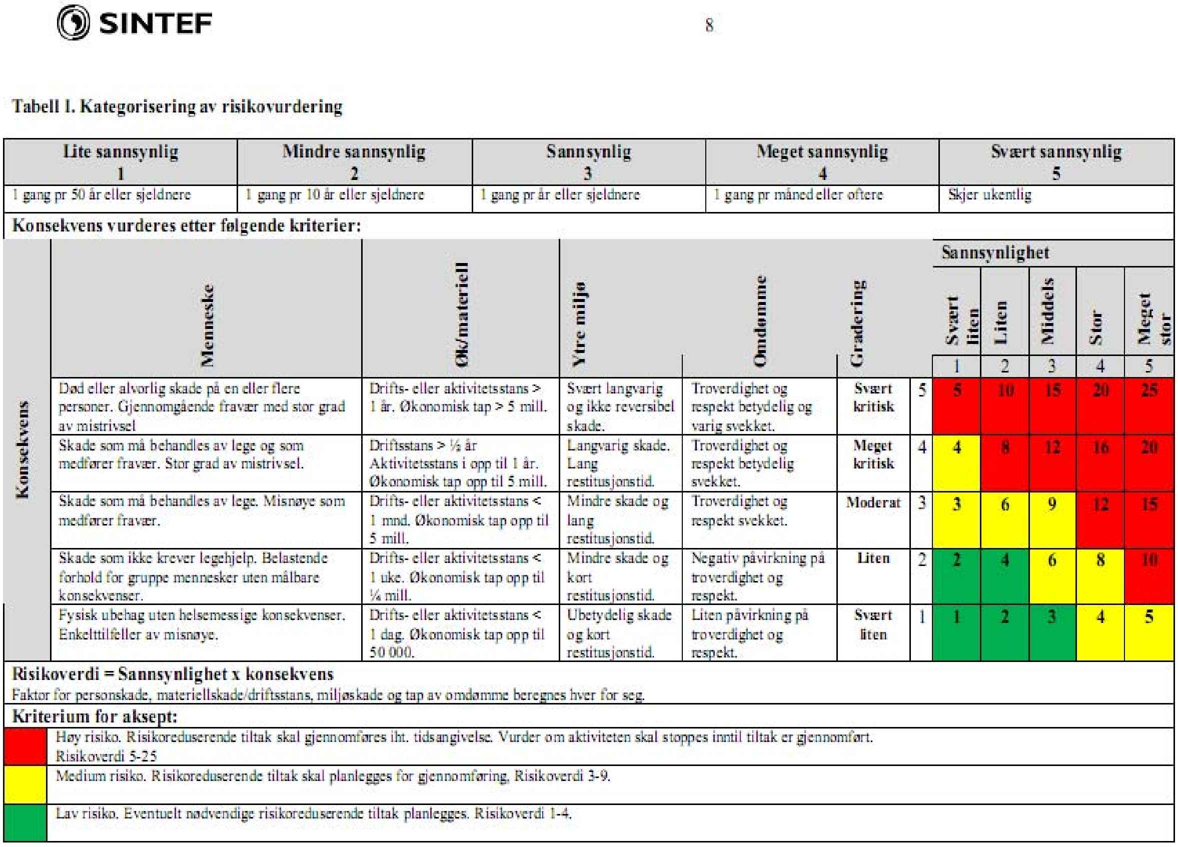
7.5 Risikovurderingens metode

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 1. 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:

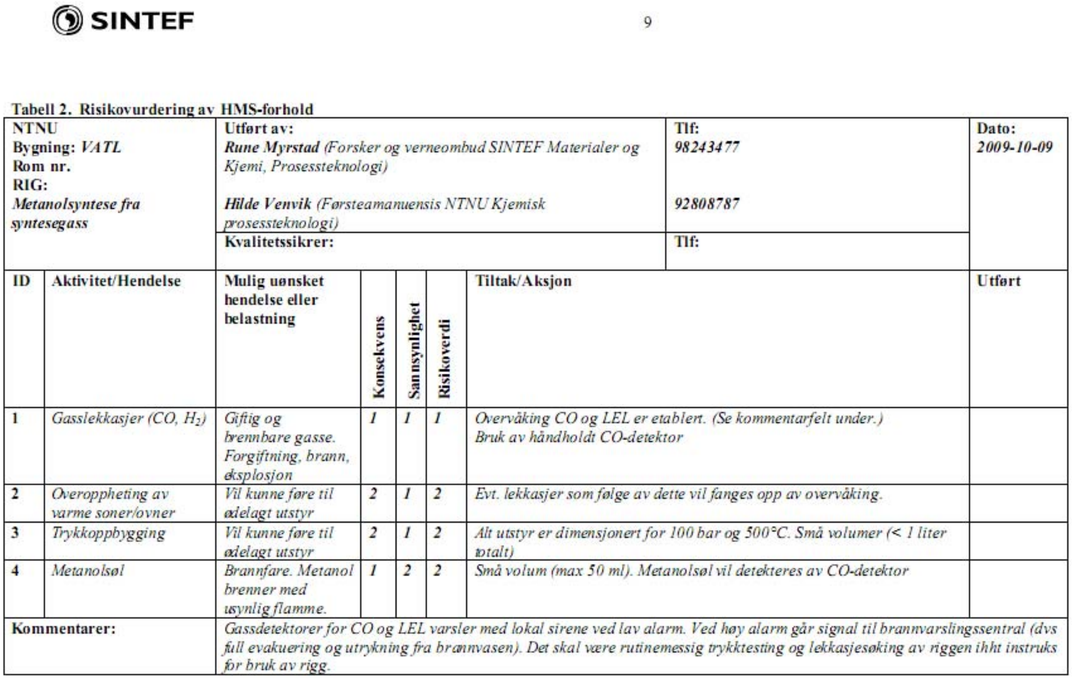
Konsekvens	Menneske	Øk/materiell	Ytre miljø	Omdømme	Gradering		Sannsynlighet Svært liten 1	Liten 2	Middels 3	Stor 4	Meget stor 5
	Død eller alvorlig skade på en eller flere personer. Gjennomgående fravær med stor grad av mistrivsel	Drifts- eller aktivitetsstans > 1 år. Økonomisk tap > 5 mill.	Svært langvarig 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.



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 gasse. 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.*					

Appendix F

The materials, safety and data sheets for all the gas and chemical are given in bellow

Conforms to 91/155/EEC - 2001/58/EC - Norway

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

Company/undertaking identification

Manufacturer / Supplier :
Yara Industrial AS
P.O.Box 23 Haugenstua
N-0915 Oslo
Norway
T: +47 22 10 64 10
F: +47 22 10 04 21

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

2. 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

*** Occupational Exposure Limit(s), if available, are listed in Section 8**

3. Hazards identification

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

Classification : R12- Extremely flammable.

Physical/chemical hazards : Extremely flammable.

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

4. First aid measures

Inhalation : If inhaled, remove to fresh air.

Ingestion : Not applicable

Skin Contact : Not applicable

Eye contact : Not applicable

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.

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

Fire-fighters should wear self-contained positive pressure breathing apparatus (SCBA) and full turnout gear.

6. Accidental release measures

Personal Precautions : Use suitable protective equipment (Section 8). Follow all fire fighting procedures (Section 5).

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, minimize ignition sources. Use explosion-proof electrical (ventilating, lighting and material handling) equipment.

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.

8. Exposure controls/personal protection

Ingredient name	Occupational exposure limits
Hydrogen	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 or gauntlets 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 : Not applicable.

Skin protection : Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.

9. Physical and chemical properties

General information

Appearance

Physical state : Gas.

Colour : Colourless.

Odour : Odourless.

Important health, safety and environmental information

Boiling point : -253.1°C (-423.6°F)

Melting point : -259.1°C (-434.4°F)

Flammability (solid, gas) : Extremely flammable gas.

Relative density : 0.071 g/cm^3

Vapor density : 0.07 (Air = 1)

Other information

Auto-ignition temperature : 399.9 to 573.8°C (751.8 to 1064.8°F)

10. Stability and reactivity

Stability : The product is stable.

11. Toxicological information

Potential acute health effects

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

12. Ecological information

Other adverse effects : The product is not expected to harm the environment when used properly according to directions.

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	2.1	Not available.		**Hazard identification number** 23
IMDG Class	UN1049	HYDROGEN, COMPRESSED	2.1	Not available.		**Emergency schedules (EmS)** F-D; S-U
IATA-DGR Class	UN1049	HYDROGEN, COMPRESSED	2.1	Not available.		Not available.

15. Regulatory information

EU Regulations

Hazard symbol(s) :

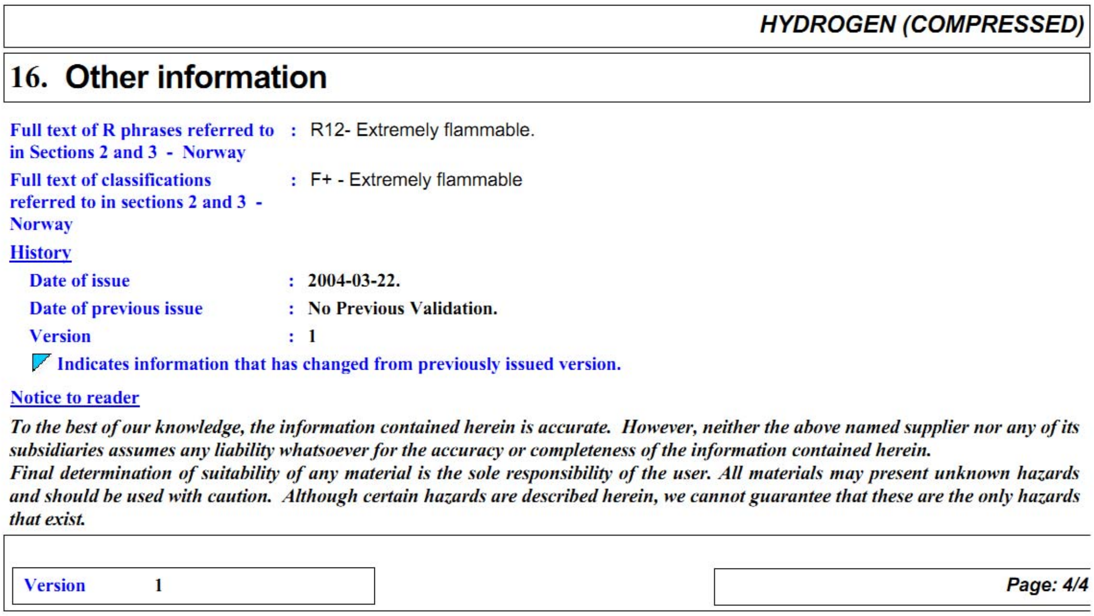
Extremely flammable

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.

OAR group : Not applicable.



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

History

Date of issue : **2004-03-22.**

Date of previous issue : **No Previous Validation.**

Version : **1**

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

Notice to reader

To the best of our knowledge, the information contained herein is accurate. However, neither the above named supplier nor any of its subsidiaries assumes any liability whatsoever for the accuracy or completeness of the information contained herein.
Final determination of suitability of any material is the sole responsibility of the user. All materials may present unknown hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards that exist.

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.

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	630-08-0	100	211-128-3	F+; R12 [1] [2] Repr. Cat. 1; R61 T; R23, R48/23
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	: 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/cm³ : 0.0012 g/cm³ (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

Date of printing : 31.12.2007.
Date of issue/Date of revision : 28.12.2007.
Date of previous issue : 04.10.2006.
Version : 3
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

METHANE

---

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

History

Date of printing : **31.12.2007.**

16. Other information

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Date of previous issue : **04.10.2006.**

Version : **3**

Prepared by : Yara Product Classification and Regulations

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

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Conforms to EU Directive 91/155/EEC, as amended by 2001/58/EC - Norway

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; met

Chemical formula : C-H4-O

Product registration number : 56212

Company/undertaking identification

Manufacturer / Supplier :

Yara Industrial AS
P.O.Box 23 Haugenstua
N-0915 Oslo
Norway
T: +47 24 15 76 00
F: +47 24 15 75 01

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

2. Composition/information on ingredients

Substance/preparation : Substance

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

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

3. Hazards identification

The substance 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.

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 : In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention immediately.

4. First-aid measures

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

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.

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.

Fire-fighters should wear self-contained positive pressure breathing apparatus (SCBA) and full turnout gear.

Hazardous thermal decomposition products : These products are carbon oxides (CO, CO_2).

6. Accidental release measures

Personal precautions : Immediately contact emergency personnel. Eliminate all ignition sources. Keep unnecessary personnel away. Use suitable protective equipment (section 8). Follow all fire-fighting procedures (section 5). Do not touch or walk through spilt material.

Environmental precautions and clean-up methods : Avoid contact of spilled material and runoff with soil and water courses.

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 it 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).

8. Exposure controls/personal protection

Ingredient name	Occupational exposure limits
Methanol	**Arbeidstilsynet (Norway, 10/2003). Skin** AN: 130 mg/m^3 8 hour(s). Form: All forms AN: 100 ppm 8 hour(s). Form: All forms

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 hour(s) (breakthrough time): butyl rubber, PTFE, Viton

Eye protection : Recommended: splash goggles
Possible: face shield

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.
Body: Recommended: overall, safety apron
Feet: Recommended: butyl rubber, PTFE, Viton
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: 15.9°C (60.6°F).

Density g/cm^3 : 0.7915 g/cm^3

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).

Hazardous decomposition products : These products are carbon oxides (CO, CO_2).

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.

Acute toxicity

Ingredient name	Test	Result	Route	Species
Methanol	LD50	5628 mg/kg	Oral	Rat
	LD50	14200 mg/kg	Oral	Rabbit
	LD50	7300 mg/kg	Oral	Mouse
	LD50	15800 mg/kg	Dermal	Rabbit
	LDLo	143 mg/kg	Oral	human
	LDLo	428 mg/kg	Oral	human
	LDLo	6422 mg/kg	Oral	man
	LDLo	393 mg/kg	Dermal	Monkey

Over-exposure signs/symptoms

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

Ecotoxicity data

Ingredient name	Species	Period	Result
Methanol	Daphnia magna (EC50)	48 hour(s)	>10000 mg/l
	Oncorhynchus mykiss (EC50)	48 hour(s)	13200 mg/l
	Lepomis macrochirus (EC50)	48 hour(s)	16000 mg/l
	Daphnia magna (LC50)	96 hour(s)	>100 mg/l
	Pimephales promelas (LC50)	96 hour(s)	>100 mg/l
	Lepomis macrochirus (LC50)	96 hour(s)	15400 mg/l

Adverse effects : The product is not expected to harm the environment when used properly according to directions.

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.

Other EU regulations

Child protection : Yes, applicable.

Tactile warning of danger : Yes, applicable.

National regulations

Hazard symbol/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

History

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

Date of previous issue : **2005-11-03.**

Version : **2.01**

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

Notice to reader

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Appendix G

Regarding to the HES I did the following courses and training

Appendix G.1: A special training course for VLT that I have done.

1879613100

TRAINOR

Certificate

of core competence awarded September 15th 2010 to

Mahmud Alam

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 1879613100, 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

Figure G- 1: certificate of VTL safety Course

Appendix G.2: A gas training course for using gas bottle in lab that I have done. The necessary documents for that are shown in bellow.

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

NTNU
Det skapende universitet

-------- Original Message --------

Subject:HSE-Security course 6. Sept.

Date: Fri, 10 Sep 2010 14:30:25 +0200

From: Berit Borthen <berit.borthen@chemeng.ntnu.no>

Reply-To:berit.borthen@chemeng.ntnu.no

Organization:NTNU

To: Hilde Johnsen Venvik <hilde.venvik@chemeng.ntnu.no>, Anders Holmen <anders.holmen@chemeng.ntnu.no>

Hei,

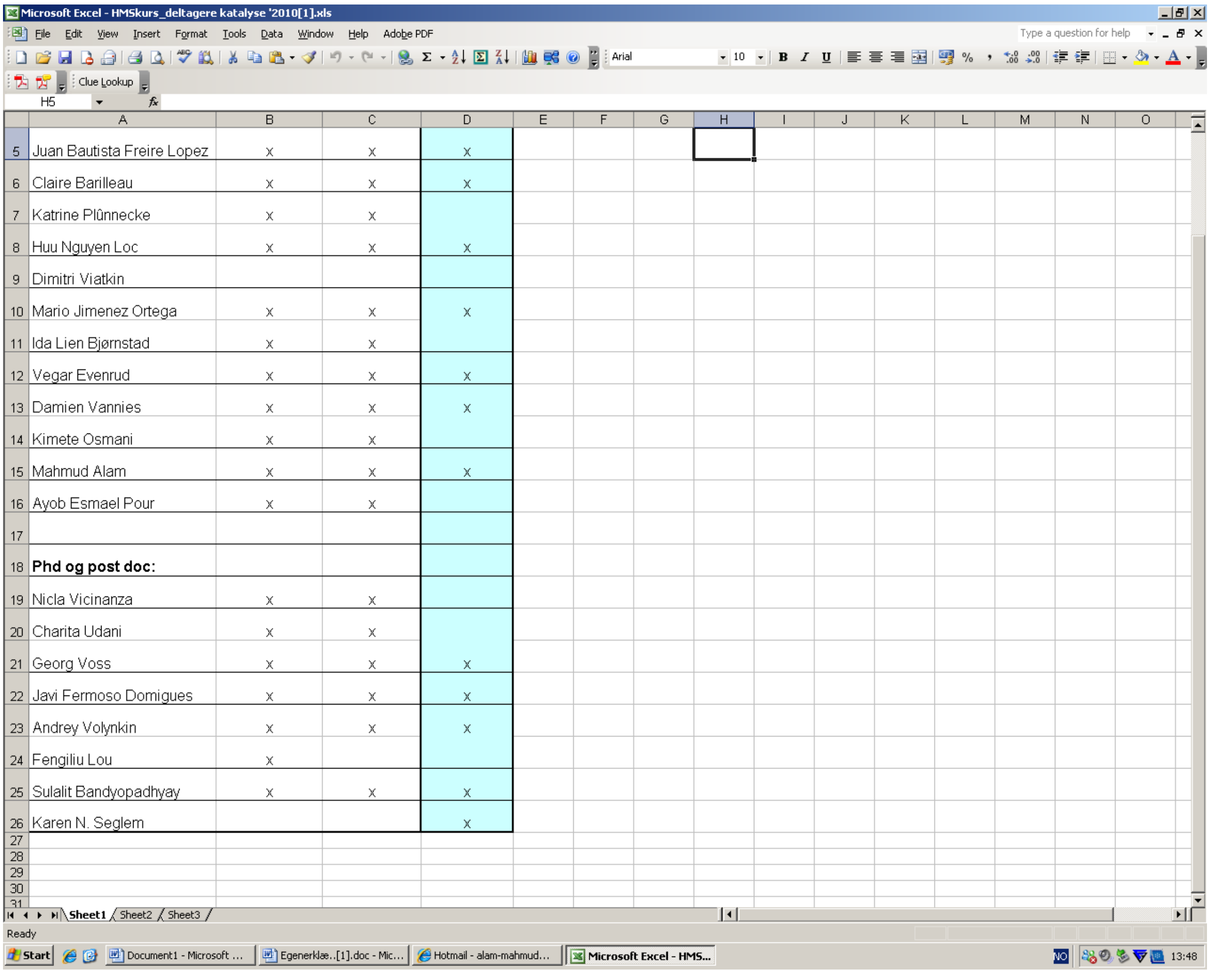
Det bekreftes herved at følgende studenter har gjennomgått IKPs HMS-introduksjonskurs.

Dette omfatter sikkerhetskurset og opplæring i bruk av gass og flaskeregulatorer. Varighet ca 2 timer.

Se vedlegg.

mvh

Berit



	A	B	C	D
5	Juan Bautista Freire Lopez	x	x	x
6	Claire Barilleau	x	x	x
7	Katrine Plûnnecke	x	x	
8	Huu Nguyen Loc	x	x	x
9	Dimitri Viatkin			
10	Mario Jimenez Ortega	x	x	x
11	Ida Lien Bjørnstad	x	x	
12	Vegar Evenrud	x	x	x
13	Damien Vannies	x	x	x
14	Kimete Osmani	x	x	
15	Mahmud Alam	x	x	x
16	Ayob Esmael Pour	x	x	
17				
18	**Phd og post doc:**			
19	Nicla Vicinanza	x	x	
20	Charita Udani	x	x	
21	Georg Voss	x	x	x
22	Javi Fermoso Domigues	x	x	x
23	Andrey Volynkin	x	x	x
24	Fengiliu Lou	x		
25	Sulalit Bandyopadhyay	x	x	x
26	Karen N. Seglem			x
27				
28				
29				
30				
31				

Figure G- 2: Above documents shows that I did a gas course 6th Sept, 2010