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Methanol Synthesis Chemistry and Process Engineering Aspects- A Review with Consequence to Botswana Chemical Industries

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Abstract

In a highly competitive world of commercial production of methanol, it is critical to understand and get methanol (CH_3OH) synthesis chemistry and process engineering aspects of methanol production correctly. Methanol synthesis chemistry knowledge is invaluable as it is applied throughout the whole process of process design, plant design, optimization and during operation of methanol plant. A comprehensive review of methanol synthesis chemistry- for synthesizing methanol from syngas (containing CO_2 , CO and H_2) over Cu- based catalyst and engineering aspects are covered in this review paper. The paper provides an overview of the chemistry behind synthesis of methanol (via hydrogenation of carbon oxides, CO and CO_2 , and water gas shift reaction), kinetics and thermodynamics of low pressure process and process engineering aspects of methanol synthesis, it also assesses the technical practicality of using low sulphur, sub- bituminous coal from Botswana to produce methanol.

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1 Introduction

Production of methanol (CH_3OH) from synthesis (syngas) has become more important as it is used as a feedstock for production of other chemicals [1–7]. Its largest use is its oxidation to formaldehyde, conversion to acetic acid and methyl tertiary butyl ether (MTBE) [8–11]. Another trend is growing demand in transportation industry, where it is blended with gasoline to increase octane ratings [1,12–15], or used directly in methanol fuel cells. Among other several uses, it is also used in Methanol to Olefins (MTO) process, then polymerization processes [16].

Industrially, methanol synthesis is carried out in gas- solid catalytic reactors, over copper-based catalysts $CuO/ZnO/Al_2O_3$ at 250 °C–300 °C and 50–100 bar via low pressure process [17,18,19]. Principal reactions in methanol synthesis are; (1) reaction of carbon monoxide with hydrogen, (2) reaction of carbon dioxide with hydrogen, (3) water- gas shift reaction, and the feed to the reactor should have a stoichiometric ratio ($H_2 - CO_2/CO + CO_2$) of 2:1 [20,21–27]. Hydrogenation of CO_2 and CO at equilibrium was shown to have a positive dependence on pressure and an inverse dependence on temperature [1,13]. Syngas (derived from carbon bearing matter i.e. natural gas, biomass or coal) is used as the feedstock to produce methanol [12,28–32].

Methanol synthesis from syngas has been of interest to academia and researchers in industries as it provides an alternative method of producing transportation fuel and feedstock for production of other chemicals. Figure 1 depicts an overview of the whole methanol production process. It consists of three main sections, gasification of carbon bearing matter to produce syngas, methanol synthesis and product upgrading. Natural gas is widely used as the raw material for production of syngas, as it has low sulphur content and other undesirable impurities [33]. However, after advancement of purification technology and discovery of low sulphur coal, coal has become the second largest source of syngas used to produce methanol [34]. The process involves selection of suitable coal gasifiers, reactors, other process equipment and optimization of process conditions (temperature and pressure) to achieve high conversion and quality of methanol. Despite having advanced technology to feasibly convert coal to methanol, Botswana has not taken advantage of having abundant coal to invest in coal to liquids e.g. coal to methanol.

There is abundant coal in Botswana (in excess of 200 billion tons) that has to be fully exploited to produce methanol and other liquid fuels. Coal from Botswana (mainly from Morupule coal mine as the sole supplier) is classified as low Sulphur and sub- bituminous coal, which is suitable for clean coal to methanol process. So, if methanol is produced from Botswana coal is expected to unlock other potential opportunities to produce other chemicals. Consequently, this will improve the economic situation of the country and revitalize the economy. The following sections provide information on chemistry behind methanol synthesis, quantity and quality of Botswana coal reserves and technology available to transform Botswana coal to methanol.

2 Methanol production process

Methanol production process starts with gasification of any solid carbon bearing matter i.e. coal, biomass or reforming of natural gas, to produce syngas (CO , CO_2 and H_2) which is later used in the process to produce methanol via catalytic synthesis over Cu- based catalyst. Downstream of methanol synthesis is methanol purification stage where methanol is purified according to specifications from customers and other needs from the chemical industry. Figure 1 below shows overview of methanol production process and production of other chemicals from methanol.

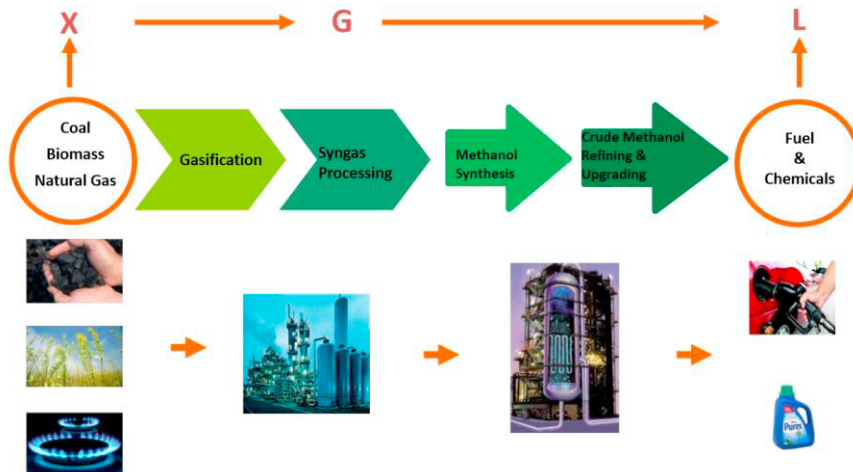


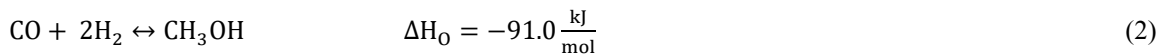
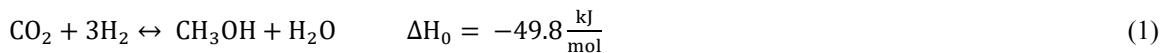
Figure 1: Overview of methanol production process [35].

2.1 Principal reactions, kinetics and thermodynamics of low pressure process

2.1.1 Principal chemical reactions

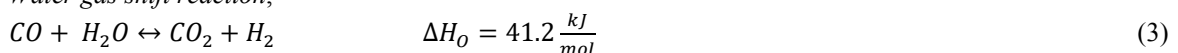
Industrially, methanol is basically produced by hydrogenation of CO and CO_2 over an active $CuO/ZnO/Al_2O_3$ catalyst via low pressure process [2,14,36–39]. The process embodies three basic steps; gasification to produce syngas, synthesis of methanol and purification of methanol.

Hydrogenation of carbon oxides,



Hydrogenation of CO and CO_2 is exothermic and reversible, so significant cooling is required to remove excess heat of reaction to shift equilibrium to produce more methanol. However, kinetics of the reactions are not favoured at lower temperatures, so optimum temperature, higher pressure and active Cu- based catalysts have to be used to obtain high conversions syngas to methanol [40,41]. The composition of the syngas/ feed is characterized by stoichiometric number ($S, H_2 - CO_2/CO + CO_2$) of 2: 1, The ratio plays a critical role in efficient production of methanol [41]. It is used to determine the optimum syngas components ratio in feed to efficiently produce methanol. According to Palma et al. [15] stoichiometric number slightly larger than 2 appears to be optimal for most of catalysts used in industrial production of methanol. The stoichiometric number was shown to depend on the type of carbon bearing material used to produce syngas [1,42]. Another important reaction in synthesis of methanol is water- gas shift reaction shown in equation 3.

Water gas shift reaction,



Equation 3 resembles water- gas shift (WGS) activity. WGS is industrially used to adjust CO_2/H_2 ratio in syngas (feedstock for methanol synthesis) [10].

2.1.2 Kinetics of low- pressure methanol synthesis

Kinetics of the process were investigated by many authors (Klier et al., 1981; Chinchén et al., 1984; Kuznetsov et al., 1984; Villa et al., 1985; Tagawa et al., 1985; Tagakawa and Ohsugi, 1987; Graaf et al., 1988; Gasser and Baiker,

1989; Skrzypek et al., 1991; Lee et al., 1993; Kuechen and Hoffmann, 1993; Waugh, 1992 in the past years [43].

2.1.2.1 Rate Equations for Production of Methanol

According to Agachi et al., [44], Natta et al., (1955) the step determining the rate of reaction is for the reaction between the species adsorbed on the surface of the catalyst pores, and they should be having the activation energy of 17.1 kcal/mol. Expressions found in literature for methanol synthesis are as shown below in Table 1.

Table 2: Kinetic rate expression proposed by different authors in literature [44].

Atroschenko, Zasorin	$r_1 = k_1 P_{H_2}^4 \sqrt{\frac{P_{CO}}{P_{CH_3OH}}} - k_2 \sqrt{\frac{P_{CH_3OH}}{P_{CO}}}$
Natta, Pasquon	$r_1 = \frac{f_{CO} P_{CO} f_{H_2}^2 P_{H_2}^2 - f_{CH_3OH} \frac{P_{CH_3OH}}{K_{cg}}}{A(1 - B f_{CO} P_{CO} + C f_{H_2}^2 P_{H_2}^2 + D f_{CH_3OH} P_{CH_3OH} + E f_{CO_2} P_{CO_2})}$
Uchida, Ogino	$r_1 = k_1 \left[\sqrt[4]{P_{CO} P_{H_2}^2} - \frac{P_{CH_3OH}}{k_{P_1} \sqrt[3]{P_{CO} P_{H_2}^2}} \right]$
Cappelli	$r_1 = k_1 \left(\frac{P_{H_2} \sqrt{P_{CO}}}{\sqrt[3]{P_{CH_3OH}^2}} - \frac{\sqrt[3]{P_{CH_3OH}}}{k_{P_1} P_{H_2} \sqrt{P_{CO}}} \right)$
Siminiceanu	$r_1 = k_2 \frac{(P_{CO_2} P_{H_2} K_{P_2} - P_{CO} P_{H_2O})}{k' P_{CO} + P_{CO_2}}$
Experimentally determined by ICI catalyser:	$r_1 = k_1 \left[\frac{P_{H_2} \sqrt{P_{CO}}}{\sqrt[3]{P_{CH_3OH}^2}} - \frac{1}{k_{P_1} P_{H_2} \sqrt{P_{CO}}} \sqrt[3]{P_{CH_3OH}^2} \right]$

Where $k_1 = 9.24 \times 10^6 e^{-11423.1/T}$

2.1.3 Thermodynamics of the reactions

Hydrogenation of CO and CO₂ to methanol is exothermic, so their conversion to methanol is not favoured at high temperatures. The enthalpy change for hydrogenation of CO₂ to methanol was found to be $\Delta H_{298K} = -48.98 \text{ kJ/mol}$, which is highly exothermic [19]. The heat of reaction has to be continuously removed from the reactor to shift equilibrium towards production of methanol. However, reducing the temperature of the process is not kinetically desirable as it slows reaction rate [45]. So, a compromise must be struck between operating at high temperatures to increase the reaction rate and low temperatures to increase conversion. This obstacle is overcome by using reactors with recycle to achieve 100% conversion [19]. However, at high temperatures reverse water-gas shift reaction (RWGS) is dominant, it is endothermic and pressure-independent, so the enthalpy change is +41.16 at 298 K [19, 46].

2.2 Methanol from Botswana coal

2.2.1 Botswana coal resources

Currently, Botswana has abundant and largely unexploited coal resources known to be in excess of 200 billion tons [47]. Morupule coal mine is the only mine mining coal for production of electricity and the excess coal is exported to neighbouring countries. The mine is positioning itself to ramp up production to 3 million tons annually, which is still insignificant compared to the available coal resources. All known Botswana coal deposits are shown in figure 7, coal resources cover almost more than 70% of the country.

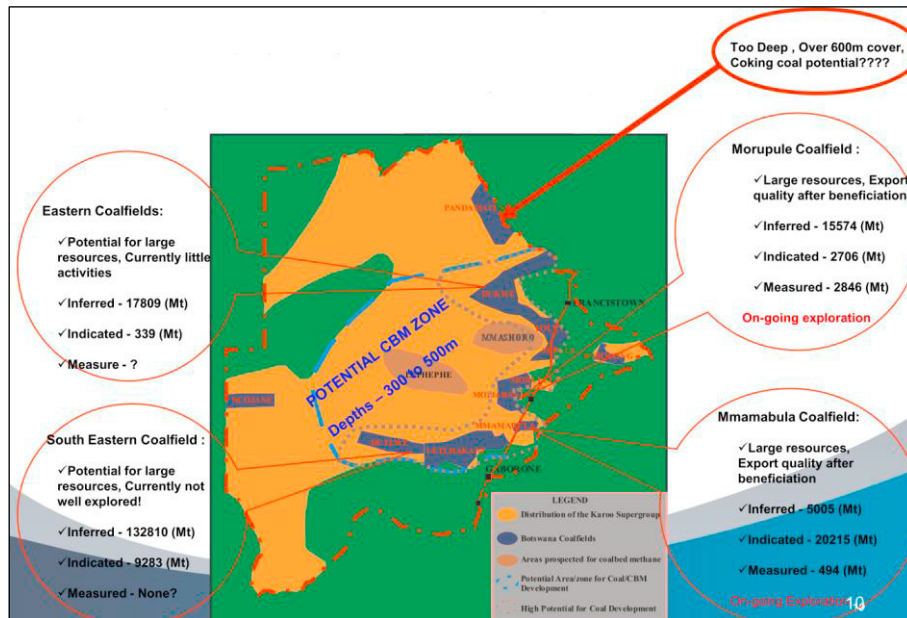


Figure 2: showing significant coal resources explored by different companies in Botswana [47].

2.2.1.1 Quality of Botswana coal and characteristics for gasification

Low rank coal is generally preferred as a feedstock for commercially available coal gasifiers used to produce syngas for methanol production [48]. That is because it has high reactivity compared to high rank coal, other desirable characteristics are low sulphur, moisture and volatile content as they are diluent of carbon in low rank coal. The quality of coal mined at Morupule coal mine good, it is low sulphur sub-bituminous coal suitable for production of syngas used in production of methanol. An international system used to classify coal is by American Society for Testing and Materials (ASTM) as shown in Table 1. The system classifies coal on the basis of caloric value, ash content, volatile matter and fixed carbon content. Ultimate analyses (analyses for carbon, sulphur, oxygen, hydrogen, nitrogen, ash and moisture contents of a coal) may be used to determine the suitability of coal for a particular purpose, e.g. for gasification of coal, and to determine processes to be used to reduce environmental pollution [49].

Table 1: The quality of coal Botswana coals compared with well-known reference brands [47].

	Botswana (High)	Botswana (Low)	Newcastle Benchmark	Richards Bay Benchmark
Energy kcal/kg	6000	5400	6322	6300
Total moisture %(ar)	8	10	15 (max)	15 (max)
Inherent moisture %(ad)	4	5		
Ash content %(ad)	13	20	14 (max)	16 (max)
Fixed carbon (ad)	58	50		
Total sulphur %(ad)	0.45	0.8	<0.75	<1.0

2.2.2 Process for production of methanol from Botswana coal

Methanol production from coal starts with gasification of coal. Gasification of coal converts coal to gaseous stream known as syngas, so coal is heated in presence of little or no oxygen to produce syngas in a coal gasifier. Phase two of the process is conversion of synthetic gas to methanol (this stage utilizes the catalyst, so process conditions depends on technology used, catalyst and the equipment used) and phase three is distillation of methanol to produce pure grade methanol depending on market requirements.

2.2.2.1 Gasification of Botswana coal

In practice, gasification of coal is achieved by converting carbon in coal to combustible gases in the presence of little or no oxygen and steam [50]. Gasification is driven by reaction of pure oxygen or oxygen in a mixture of air with carbon and steam at temperatures above 800 °C and pressures above 20 MPa depending on the type of gasifier used to produce medium heating value syngas, and pressure requirements upstream of the process. Gasification technologies are categorized according to the configuration of the reactor bed. The categories are fluidized bed, fixed bed, molten salt and entrained bed. Detailed description of each type of gasification reactor can be found at [51]. Table 2 shows performance of major gasification plants after using low rank coal, all gasification plants have very high carbon efficiency (< 90 %) and high volume of $CO + H_2$.

Table 2: Performance of major coal gasification plants [52].

Parameter	Vendors/ licensors					
	Shell SCGP	Siemen/ GSP	Lurgi (Mark V)	ECUST OMB	HT-L	GE- energy
Raw syngas (dry) (km ³ (std/h)	187- 206	132- 142		159- 185	119- 131	
Raw gas composition						
CO (vol%)	60- 65	65- 75	16- 28	61.6	61.9	39/ 45
H ₂ (vol%)	23.84;18-23;30	20- 28	38- 40	30.24;37.6	26.3	38; 36.63
CO ₂ (vol%)	3.84;2-3;1.6	4- 5	27- 32	16.5; 4.51	8.2	21; 17.69
H ₂ O (vol%)				0.1		
CH ₄ (vol%)	100-200 ppm	0.05- 0.1	7-2; 16- 18		756 ppm	0.09
H ₂ S (vol%)	0.3					
Dry coal input (t/h)	2000- 2850	2000- 2300	1800	2500-3000	1800	2000
Operating pressure (MPa)	2.0- 4.0	2.5- 4.2	3.0-5.0	3.0- 6.5	3.7- 4.0	4.0-6.5; 8.7
Maximum gasification temperature (°C)	1400- 1600	1350- 1750		1300-1400	1400-1750	1300- 1400
CO + H ₂ (vol%)	90- 94	92- 95	65	77; 81- 83.4	86- 92	78- 81
Coal consumption (kg/kNm ³) (H ₂ +CO)	635	653		693	640	
Oxygen consumption (kg/kNm ³) (H ₂ +CO)	320;330-360	331	160- 270	432	322	380- 430
Cold gas efficiency (%)	80- 85	78- 85	65- 75	70- 76	75- 84	70- 76
Carbon efficiency (%)	>99	98- 99	88- 95	98.6- 99.1	98- 99.5	96- 98
Thermal efficiency (%)	98	90			95- 96	90-95

2.2.3 Industrially available methanol synthesis reactors

Commercially, there are two types of reactors commonly used for production of methanol today, the reactors are adiabatic and isothermal from a category of gas phase reactors [53]. Methanol synthesis is exothermic, so these reactors are designed to efficiently control the temperature. Adiabatic reactors typically have a series of fixed bed reactors with heat exchangers to remove heat of reaction, they have low installation cost and high production capacity [53]. However, operation of adiabatic reactors is characterized by low conversion per cycle caused by high equilibrium temperatures, high recycle ratio, high dilution of reactants and high volume of catalyst used.

Isothermal reactors are continuously cooled by external fluid stream, either water or gas cooled, they have the same configuration as heat exchangers. Isothermal characteristics of the design enables high conversion and low volume usage of catalyst. However, the installation costs are reported to be higher than that of adiabatic reactors and the size of the plant is limited by tube bundles [15]. So isothermal reactors are widely used in industrial production of methanol. The reactors were customized by several manufacturers such as Topsoe, Lurgi, Linde and Mitsubishi Heavy Industries

[53].

2.3 Developments in the process engineering aspects of methanol production

2.4.1. Optimal control of methanol reactors: using Pontryagin Maximum Principle

Optimal control of methanol synthesis reactors is critical in methanol industry, the need for optimal control of reactors was recognized since 1980s due to the pressing need to reduce raw material losses and to minimize energy costs [56,57]. It aims to optimize one or many desired objective functions such as the economic benefit, conversion rate of raw materials, time taken to complete batch process or the return on the investment in methanol production [56]. In steady state control, Pontryagin maximum principle was developed by Russian mathematician Pontryagin in 1956. The principle was successfully applied by Agachi [44] on methanol synthesis plant at C.C. Victoria, Romania to control the temperature profile. In their calculations they anticipated 33.8 % increase in production, but in practice 27 % increase was achieved, details on applying Pontryagin maximum principle can be found at [30,44,59].

2.4.2. Adaptive control of $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst deactivation

Decrease in catalyst selectivity and/or activity is a major problem in methanol synthesis industry, being able to predict the catalyst deactivation behaviour and counteract it renders the operation profitable. Cu- based catalyst deactivation is known to be mainly caused by poisoning by sulphur, chlorine compounds, formation of metal carbonyls and excess of CO_2 and H_2O and thermal sintering caused by high temperature [58]. Deactivation of Cu- based catalyst is practically controlled by good engineering practices, removal of poisoning impurities (e.g. Sulphur, chlorine and others) from syngas, modification and proper formulation of $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst to give increased resistance to poisoning, thermal sintering and increased stability [59]. Table 3 shows catalyst deactivation and measures taken to counteract it.

Table 3: Deactivation of the catalyst and measures to slow deactivation [60].

Process	Catalyst	Main deactivation mechanism	Time scale of deactivation	Consequence for catalyst	Consequence for process
Catalytic reforming	Pt/ γ - Al_2O_3	Coke	Months	Alloying	Fixed bed, swing operation, moving bed
Hydrotreating	Co/Mo/S/ Al_2O_3	Coke Metal sulphides	Months Dyas	Once through cat. Adapted porosity	Fixed bed, slurry, moving bed
Methanol	$\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$	Sintering (CI)	Years	Stabilization	Feed purification
Water- gas shift	$\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$	Poisoning (S, CI)	Years	Stabilizers (ZnO)	Feed purification
Steam reforming	Ni/ Al_2O_3	Coke, whiskers		K, Mg gasification	Excess steam
Dry reforming	Ni	Coke		Catalysts	
				S- doping	Excess steam

Riaz et al. [60] indicated that the major causes of catalyst deactivation is thermal sintering caused by poor heat transfer in methanol synthesis reactors. The final deactivation model for a sparged slurry reactor operating at 250 °C and 53 bar was found to be first order;

$-\frac{ds}{dt} = ks^n$ where, S is active metal surface area. For a fixed bed reactor, the model equation is;

$$\frac{da}{dt} = -K_d \exp\left(-\frac{E_d}{R_g}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)a^5 \quad (4)$$

Where values of E_d and K_d were reported to be 9.1×10^4 J/mol and $4.39 \times 10^{-5} \text{ h}^{-1}$ respectively [60].

When considering the effect of CO/CO_2 on deactivation of Cu- based catalyst, equation 7 becomes;

$$\frac{da}{dt} = -\left(\frac{\text{CO}}{\text{CO}_2}\right)^m K_d \exp\left(-\frac{E_d}{R_g}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right)a^5 \quad (5)$$

Where m is the parameter for reaction rate.

2.4.3. Improvement of the design to increase the efficiency

Earliest methanol commercial plants utilized syngas derived from carbon bearing solid matter, mainly coal, wood or biomass. Designs of the process shared the following common processing stages; coal gasification (high pressure fixed bed or fluidized bed were preferred for large installations), syngas cooling and particulate removal, methanol production and purification [37]. Ever since commercial production of methanol, design improvements are mainly on the process stages, process conditions (pressure and temperature), composition of catalyst used, quality of syngas/feedstock, process control and the equipment used. Earliest methanol production plants operated at high pressures and temperatures (using iron, nickel or silver catalyst), it was later improved to low pressure process by using Cu/ Zn/Al oxide catalyst. Operating at low pressure was made possible by advanced syngas purification techniques, methane reforming to produce pure syngas and the use of highly selective Cu- based catalyst [61]. In terms of equipment used, the most distinguishing feature is the type of methanol converter used. Since hydrogenation of carbon oxides is exothermic, methanol converters are designed to remove heat of reaction by either using internally cooled converted or externally cooled converters [61]. Early versions of methanol converters used a single catalyst bed cooled by gas injected at multiple points down the vessel [61]. However, early design suffered from large temperature distributions. Lurgi type reactors, were used for a long time as they were able to remove heat of reaction and achieve high conversions [61].

3 Conclusion

Literature indicates that methanol synthesis proceeds via hydrogenation of both carbon oxides (CO and CO_2) and water gas shift reaction is used to adjust H_2/CO ratio. Hydrogenation of both carbon oxides is exothermic, so heat of reaction should be continuously removed from reactor to obtain high conversion of syngas to methanol. Hydrogenation of oxides also exhibit reduction in volume (moles) as reactions proceed from syngas to methanol, according to Le-Chatelier's principle, high pressure is therefore required to drive reactions towards production of methanol.

Cu- based catalysts ($Cu/ZnO/Al_2O_3$) form the backbone of low pressure process methanol synthesis process developed by ICI in 1960s. Production of methanol is highly influenced by the success of ICI technology. The process gained popularity due to high activity at low temperatures, temperatures as low as 200 °C, which consequently lowered costs in methanol synthesis process. The use of Cu- based catalyst was also favoured by development of advanced purification techniques of syngas, which otherwise would poison Cu- base catalysts with impurities.

Ever since the foundation laid by ICI process, methanol production industries are now focusing on improving efficiency of the process by developing new reactor technologies, new process schemes to minimize recycle ratio, improve and optimize temperature profile across the reactor, modify Cu- based catalysts to be more water tolerant, more active by finely dispersing active surface and to be more stable under extreme operating conditions.

Botswana coal is mainly dominated by sub- bituminous coal, suitable for gasification and methanol synthesis as it is highly reactive to combustion. Ultimate analyses of Botswana coal shows that it has desirable characteristics, low sulphur, moisture and volatile content and it compares favourably well against coal available in international markets. This present an opportunity to invest on clean coal technologies, to produce methanol and other liquid fuels. Available technologies, for low pressure process, that can be used to produce methanol from syngas produced from Botswana coal are; ICI, Lurgi, Haldor and MGC low pressure process. They are all designed to remove heat of reaction in different ways to shift the reversible equilibrium towards production of methanol.

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