

**DIRECT LIQUEFACTION OF TWO SUBBITUMINOUS COALS USING
KOH/METHANOL**

by

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Two subbituminous coals, namely Rosebud and Wyodak-Anderson, were used in the development of a non-catalytic direct coal liquefaction process employing potassium hydroxide (KOH) and methanol (CH₃OH) at high temperature. Samples from both coals were obtained from the Penn State Coal Sample Bank and Database, where Rosebud coal is from Rosebud seam, Rosebud County, Montana, USA and Wyodak-Anderson coal is from Wyodak seam, Campbell County, Wyoming, USA.

The experiments were conducted in a one-liter, high-pressure, high-temperature agitated autoclave. The effects of temperature (280, 290 and 300 °C) and coal-LiDi-methanol (C:K:M) ratio (2:1:9, 2:3:9 and 3:3:9) on the process gaseous and liquid product yields were investigated at a mixing speed of 1200 rpm. The reactor pressure and temperature were monitored and recorded throughout the experiments. At the completion of each experiment, the liquefaction products were neutralized with hydrochloric acid, washed with water, and filtered. The solid products were then subjected to the sequential selective solvent extraction technique, where n-hexane, toluene, and tetrahydrofuran were used to obtain the yield of solubles in each respective solvent. The n-hexane solubles, n-hexane insolubles/toluene solubles, toluene insolubles/THF solubles and THF insolubles measured were denoted as hexane solubles (HS), toluene solubles (TS), THF solubles (THFS) and THF insolubles (THFI), respectively.

The experimental results indicated that at high temperatures CH_3OH and KOH appeared to liquefy Rosebud and Wyodak-Anderson coals; and the effects of temperature on the process yields were found to be strongly dependent on coal type and C:K:M ratio. The highest yield of liquid products was obtained at $300\text{ }^\circ\text{C}$ and C:K:M ratio of 2:1:9, the liquid products yield obtained from Rosebud coal was higher than that from Wyodak-Anderson coal. The presence of KOH appeared to favor hydrogen production over liquid hydrocarbons production, leading to a high yield of light hydrocarbons and hydrogen and a low yield of liquid hydrocarbons. Also, the maximum total yield of liquid products obtained in this study was about 44.3 wt.% which was much lower than that reported by Shabtai and Saito [1] who obtained yield up to 90 wt.% in their base-catalyzed liquefaction process, which highlights the fundamental difference between catalytic and non-catalytic coal liquefaction processes.

TABLE OF CONTENTS

NOMENCLATURE	XII
1.0 INTRODUCTION	1
1.1 INDIRECT COAL CONVERSION (ICC).....	5
1.2 DIRECT COAL LIQUEFACTION (DCL).....	7
1.2.1 Pyrolysis.....	8
1.2.2 Solvent extraction	9
1.2.3 Catalytic liquefaction	10
1.2.4 Liquefaction using alkali/alcohol.....	12
2.0 LIQUEFACTION USING ALKALI/ALCOHOL BACKGROUND.....	13
2.1 REACTION MECHANISM.....	17
2.2 CONCEPTUAL LIQUEFACTION PROCESS USING ALKALI/ALCOHOL.	18
2.3 EFFECT OF REACTION CONDITIONS	20
3.0 OBJECTIVE	23
4.0 EXPERIMENTAL	24
4.1 EXPERIMENTAL SETUP	24
4.1.1 Non-Catalytic Direct Coal Liquefaction Process using KOH/Methanol.....	24
4.1.1.1 Reactor	25
4.1.1.2 Monitoring and data acquisition system	25
4.1.2 Sequential selective solvent extraction technique.....	27

4.2	OPERATING VARIABLES	30
4.2.1	Direct coal liquefaction.....	30
4.2.2	Operating conditions of sequential selective solvent extraction.....	31
4.3	CHEMICALS PROPERTIES.....	32
4.4	EXPERIMENTAL PROCEDURE.....	35
4.4.1	Direct coal liquefaction process using KOH/methanol	35
4.4.2	Sequential selective solvent extraction technique.....	36
5.0	CALCULATIONS.....	37
5.1	ESTIMATION OF THE PRESSURE OF SUPERCRITICAL METHANOL....	37
5.2	MATERIAL BALANCE CALCULATIONS	38
5.2.1	Volatile products yield calculation	39
5.2.2	Soluble products yield calculation.....	42
6.0	RESULTS AND DISCUSSION	43
6.1	PRESSURE EXPERIMENTAL DATA.....	43
6.2	SEQUENTIAL SELECTIVE SOLVENT EXTRACTION RESULTS	47
6.2.1	Effect of temperature on the Yields of Rosebud and Wyodak-Anderson coals	48
6.2.1.1	Effect of temperature on liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 2:1:9	48
6.2.1.2	Effect of temperature on liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 2:3:9	49
6.2.1.3	Effect of temperature on liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 3:3:9	51
6.2.2	Effect of KOH on the Yields of Rosebud and Wyodak-Anderson coals.....	52
6.2.2.1	Effect of KOH on the Yields of Rosebud and Wyodak-Anderson coals at 280 °C	52
6.2.2.2	Effect of KOH on the Yields of Rosebud and Wyodak-Anderson coals at 290 °C	53

6.2.2.3	Effect of KOH on the Yields of Rosebud and Wyodak-Anderson coals at 300 °C	54
6.2.2.4	Remarks on the effect of KOH on the Yields of both coals	55
7.0	CONCLUDING REMARKS	57
8.0	FUTURE WORK	59
	APPENDIX A	60
	APPENDIX B	69
	APPENDIX C	71
	BIBLIOGRAPHY	74

LIST OF TABLES

Table 1: Literature studies on coal liquefaction using alkali/alcohol	14
Table 2: Effect of reaction parameters on the coal liquefaction process	21
Table 3: Reactor Dimensions.....	27
Table 4: Solubles extracted by different solvents	28
Table 5: Operating variables for the direct coal liquefaction process	30
Table 6: Amount of chemicals used in Rosebud coal liquefaction experiment.....	31
Table 7: Amount of chemicals used in Wyodak-Anderson coal liquefaction experiment	31
Table 8: Elemental analysis of the coal samples	32
Table 9: Proximate analysis of the coal samples	33
Table 10: Ultimate analysis of the coal samples.....	33
Table 11: Sulfur contents of the coal samples	34
Table 12: Some details of the chemicals used	34
Table 13: Pressure and mass fraction of water in a water-methanol system	70

LIST OF FIGURES

Figure 1: Crude oil price [4]	2
Figure 2: Energy resource reserves by geographical distribution [2]	3
Figure 3: Indirect coal conversion [7].....	5
Figure 4: Hypothetical reaction schemes for coal decomposition [15]	9
Figure 5: The coal liquefaction process proposed by Shabtai and Saito [1].....	19
Figure 6: Process block diagram for coal liquefaction using alkali/alcohol.....	20
Figure 7: Experimental setup for the coal liquefaction process.....	26
Figure 8: Extraction scheme for the neutralized coal liquefaction product	29
Figure 9: Photo of the solvent extraction apparatus used	29
Figure 10: P-T behavior of supercritical methanol at different densities	38
Figure 11: Material balance block diagram	40
Figure 12: Maximum pressure observed using Rosebud coal	44
Figure 13: Maximum pressure observed using Wyodak-Anderson coal.....	45
Figure 14: Reactor pressure at ambient temperature (at the end of the run) using Rosebud coal	46
Figure 15: Reactor pressure at ambient temperature (at the end of the run) using Wyodak-Anderson coal	47
Figure 16: Effect of temperature at on the yields of Rosebud and Wyodak-Anderson coals at 2:1:9 C:K:M ratio.....	49
Figure 17: Effect of temperature at on the yields of Rosebud and Wyodak-Anderson coals at 2:3:9 C:K:M ratio.....	50

Figure 18: Effect of temperature at on the yields of Rosebud and Wyodak-Anderson coals at 3:3:9 C:K:M ratio.....	52
Figure 19: Effect of KOH on the yields of Rosebud and Wyodak-Anderson coals at 280 °C.....	53
Figure 20: Effect of KOH on the yields of Rosebud and Wyodak-Anderson coals at 290 °C.....	54
Figure 21: Effect of KOH on the yields of Rosebud and Wyodak-Anderson coals at 300 °C.....	55
Figure 22: Fractional product recovery and standard error bar for Rosebud coal	72
Figure 23: Fractional product recovery and standard error bar for Wyodak-Anderson coal.....	72
Figure 24: Maximum pressure data and standard error bar for Rosebud coal.....	73
Figure 25: Maximum pressure data and standard error bar for Wyodak-Anderson coal	73

NOMENCLATURE

m_C^o	Mass of coal as received (grams)
m_{DC}^o	Mass of dry coal feed (grams)
m_{KOH}^o	Mass of KOH feed (grams)
m_{MeOH}^o	Mass of methanol feed (grams)
S_{wi}	Moisture content of coal (weight fraction)
m_{FW}	Mass of wet reactor effluent (grams)
m_{FD}	Mass of dry reactor effluent (grams)
m_{DC}	Mass of dry coal (grams)
m_{KOH}	Mass of KOH (grams)
m_{FD_i}	Mass of dry reactor effluent sampling out for sequential selective solvent extraction (grams)
m_{DC_i}	Mass of coal used for sequential selective solvent extraction (grams)
m_{KOH_i}	Mass of KOH remain in the dry sample (grams)
$m_{DC_i}^o$	Normalized mass of dry coal feed in the sample (grams)
m_{WS}	Mass of water solubles (grams)
m_{HS}	Mass of hexane solubles (grams)
m_{TS}	Mass of toluene solubles (grams)
m_{THFS}	Mass of tetrahydrofuran solubles (grams)
C:K:M	Coal:KOH:Methanol (wt:wt:wt)

P_{Max}	Maximum pressure during the liquefaction reaction (bar)
P_f	Pressure at the end of the run (bar)
T_{Max}	Maximum temperature during the liquefaction reaction ($^{\circ}\text{C}$)
T_f	Temperature at the end of the run ($^{\circ}\text{C}$)
σ	Standard deviation

Abbreviations and acronyms

AARE	Absolute Average Relative Error
BuOK	Potassium Butoxide
C_2H_4	Ethylene
CH_3OK	Potassium Methoxide
CTL	Coal-to-Liquid
daf	Dry Ash Free
DCL	Direct Coal Liquefaction
dmmf	Dry mineral matter free
EtOH	Ethanol or ethyl alcohol
F-T	Fischer-Tropsch
FTIR	Fourier Transform Infrared Spectroscopy
HCOOK	Potassium formate
HI	n-Hexane Insolubles
HS	n-Hexane Solubles
HT	Hydrotreatment
ICC	Indirect Coal Conversion

ICL	Indirect Coal Liquefaction
K_2CO_3	Potassium carbonate
KOH	Potassium Hydroxide
MeOH or CH_3OH	Methanol or Methyl alcohol
MSDS	Material Safety Data Sheet
NaOH	Sodium Hydroxide
PrOK	Potassium Propoxide
THF	Tetrahydrofuran
THFI	Tetrahydrofuran Insoluble
THFS	Tetrahydrofuran Soluble
TI	Toluene Insolubles
TS	Toluene Solubles
WI	Water Insolubles
WS	Water Solubles

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1.0 INTRODUCTION

The U.S. has consistently been one of the largest consumers of oil worldwide, amounting 20.5% of the total world oil consumption (4,059 million tons/year) in 2011[2]. The majority of the U.S. energy consumption lies within the transportation sector, which accounts for 70% of the total oil consumption [3]. Over the last decade, oil demand has been rising in contrast with its limited supply, causing the price of crude oil to rapidly rise (Figure 1). This huge increase in worldwide demand for petroleum in recent years, in conjunction with the dwindling supply and the ever growing political instability in the Middle and Far East, will eventually lead to a worldwide energy and transportation fuel crisis in the near future. In fact, it has been predicted that the recent extreme price volatility exhibited by gasoline and diesel fuels will occur repeatedly and precariously in the near future, yet on a more drastic scale [1]. Over the past two years, the political instability in the Middle East, the drastic decline of oil production from Libya, the ripple effect on world energy markets caused by Japan and Germany's decision to move away from nuclear energy that resulted from the recent infamous Japan tsunami, the 71% increase in energy demand from China, and the poor sugar harvest from the ethanol-powered Brazil have resulted in a record hike of oil prices to around \$111 per barrel [2].

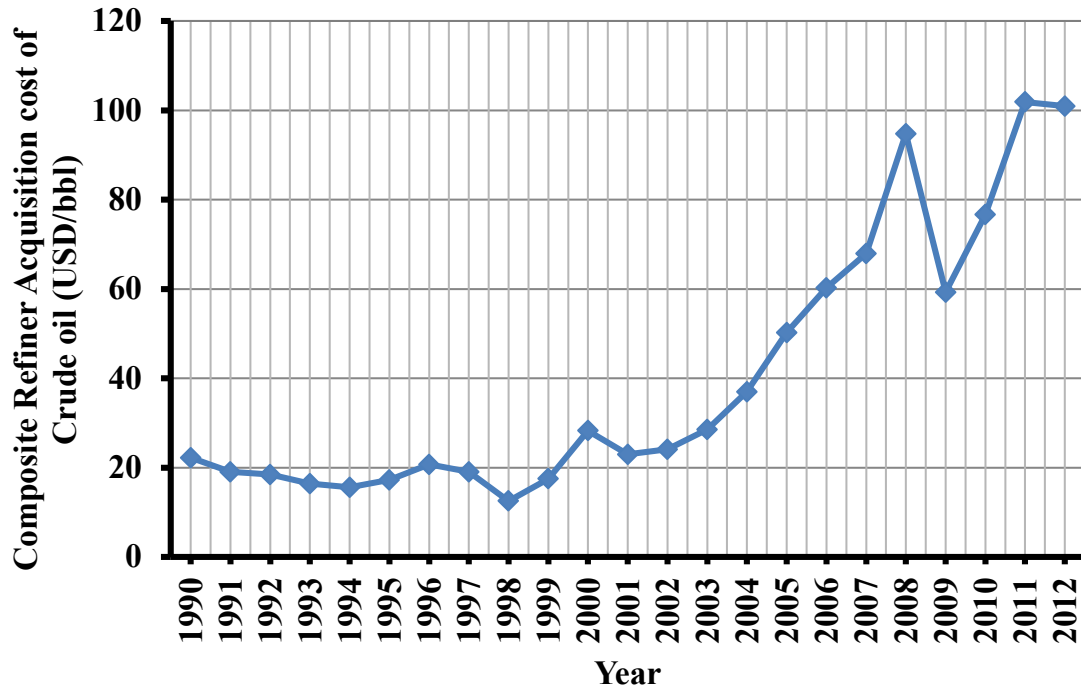


Figure 1: Crude oil price [4]

Such trends and precarious political atmospheres in crude oil producing regions have driven energy producers to seek solutions to the impending crisis by looking towards alternative energy. Although oil sand and shale gas have shown potential for being acceptable alternative energy resources, their development and production are still at the inception stage and are unable to satisfy the increasing energy demand. Another alternative solution that could fulfill the transportation sector's demand is the coal conversion process which produces transportation fuels.

Coal deposits are of particular interest in the United States and the developing countries, such as China and India. Coal is the most abundant energy source in the United States. Huge coal reserves are also available worldwide. It has been estimated in 2013 that, based on current consumption trends, proved coal reserves would be sufficient to meet 109 years of global energy

production, which is twice the number of years (52.9 years) when compared to oil [5]. Figure 2 displays the allocation of the natural gas, oil and coal resources across different geographical regions.

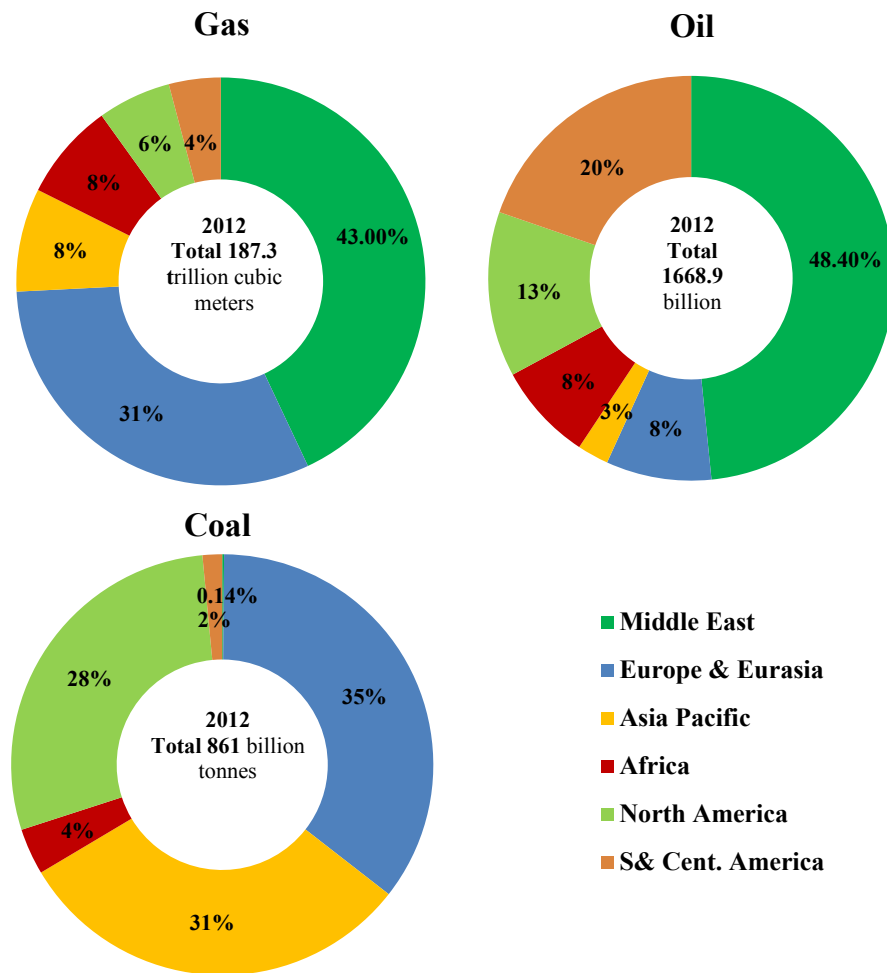


Figure 2: Energy resource reserves by geographical distribution [2]

Driven by the limited availability of cheap oil, abundance of coal and its decreasing role in electricity generation, research on direct (coal liquefaction) or indirect (coal-to-liquid, CTL) coal conversion has been increasing over the years. The Coal liquefaction process in which coal

is directly converted into liquids produces a feedstock which can be fed to existing refineries, with only minor modification. As a result, it allows related industries namely, the automobile and petrochemical industries to avoid introducing dramatic change to their operational landscapes.

Historically, coal has been primarily used as a fuel for electricity generation. Strict environmental regulations on coal combustion however, have severely limited its use in electricity generation. Moreover, the discovery of vast supplies of shale gas which led to a decrease in gas prices, has forced energy companies to either retire their coal-fired power plants or install state-of-the-art pollution control equipment [6], thus making coal-fired power plants an uneconomical and less attractive choice for electricity generation, compared to other alternatives. As more companies are moving away from utilizing coal for direct energy generation, one can expect that more coal would be available at lower price.

The research on coal conversion has been an ongoing process for the past two centuries as the emergence of coal liquefaction processes can be traced back to the early 19th century. It has been widely accepted that coal liquefaction could be successfully commercialized, if the efficiency of the process is improved, while the energy consumption and pollutant byproducts are reduced. Nevertheless, the key hindrance is the economic feasibility that relies on the price difference between coal and oil, as evident by the fact that the interest in coal conversion research, once a popular subject, has steeply declined after the discovery of cheaper oil sources in the Middle East in 1970s. With the current projected increase in oil price and subsequent drop in coal price, coal conversion has emerged, once again, as one of the attractive solutions for the energy crisis.

Coal conversion can be achieved via two principal routes: (1) Indirect Coal Conversion (ICC) and (2) Direct Coal Liquefaction (DCL).

1.1 INDIRECT COAL CONVERSION (ICC)

Indirect coal conversion (ICC) employs an indirect approach by which coal is first converted into “synthesis gas” or “syngas” (consisting primarily of CO and H₂) via reactions with steam and oxygen or air, known as gasification. After purification, the syngas is converted into liquid hydrocarbons as illustrated in Figure 3.

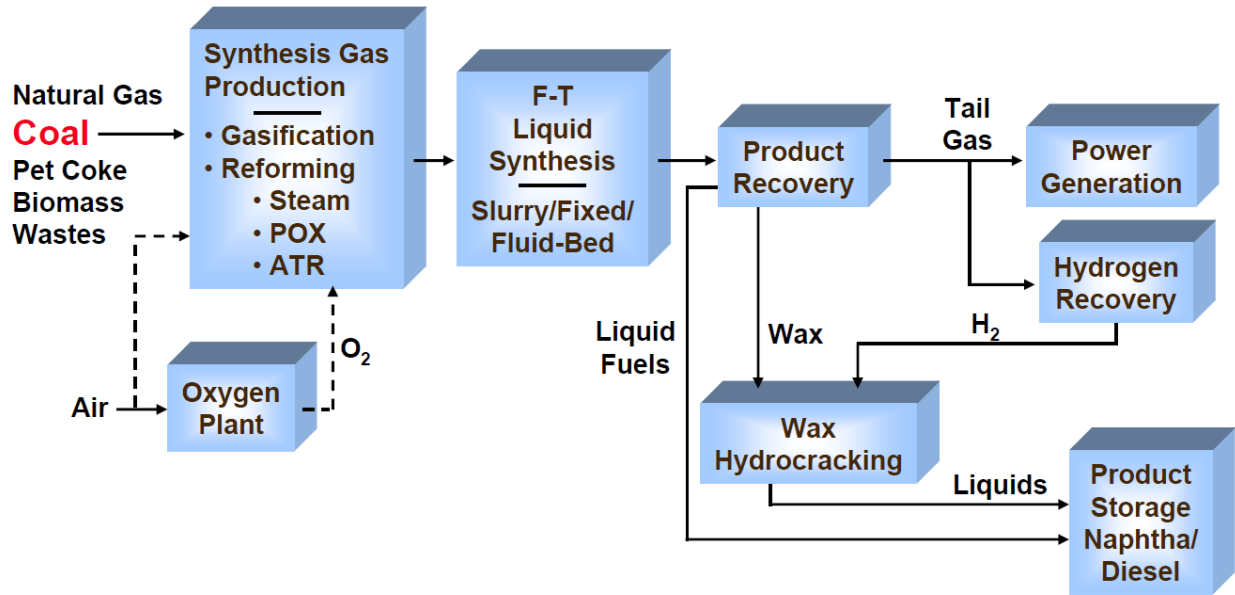
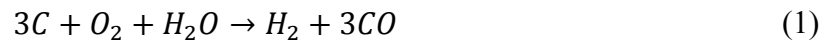


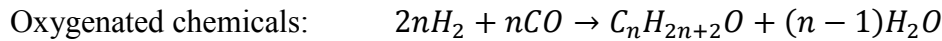
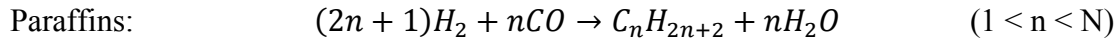
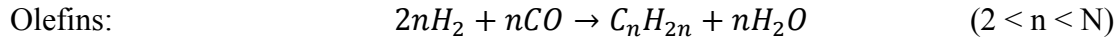
Figure 3: Indirect coal conversion [7]

The gasification is carried out at temperatures in excess of 800 °C at moderate pressure. The reaction that takes place is:



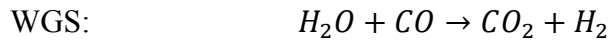
The process by which liquid hydrocarbons are produced via the catalytic reaction of carbon monoxide and hydrogen is called the Fischer-Tropsch (F-T) synthesis. The F-T synthesis produces a variety of hydrocarbons, such as paraffins, olefins and oxygenated chemicals

(alcohols, aldehydes, acids, ketones and etc...) in the presence of cobalt or iron catalysts. The main product reactions that take place in F-T synthesis are:



Where n is the average carbon number of the hydrocarbon product [8].

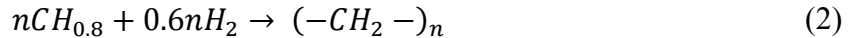
When the reaction is carried out using iron catalyst, the Water Gas Shift (WGS) reaction takes place as a side reaction.



The reaction conditions, such as temperature, pressure, type of catalyst and H₂/CO ratio strongly affect the F-T synthesis reactions. The F-T reaction conditions are typically 200 to 300 °C and 5 to 40 bar. Fischer-Tropsch synthesis is the only coal conversion liquefaction process which has been successfully commercialized. The Sasol plant in South Africa has been in operation since 1956. A comprehensive review of F-T synthesis and reactions carried out in slurry reactors has been recently published by Sehabiague and Morsi [9] and Sehabiague et al. [10].

1.2 DIRECT COAL LIQUEFACTION (DCL)

Direct coal liquefaction (DCL) is a process by which coal, a solid fuel, is converted into liquid fuel by means of adding hydrogen into or rejecting carbon from the coal molecules. The concept of the direct coal liquefaction reaction can be described as [11]:



The objectives of coal liquefaction are: (1) to break the coal structure into smaller units either by reducing the effect of weak bonds or bringing about decomposition of other key bonds, and (2) to increase the hydrogen/carbon atomic ratio from approximately 0.8 to around 1.7 or more, in order to promote the production of low-sulfur and ash-free liquid products [7]. Although the concept described above represents a simple and straight forward reaction, coal liquefaction is rather a complex process due to the lack of a realistic model representing coal structure, which limits understanding of the coal liquefaction process [11]. Thus, most coal chemical reaction studies are merely speculative.

The DCL process can be achieved via several process schemes and concepts; however, the key factors that would lead to commercialization are very much the same, which are to maximize energy efficiency and economic feasibility, while minimizing environmental impact.

The DCL process can be operated as a single stage process, having only one main reactor or series of reactors that operate at the same conditions, or as a two-stage process, by which two reactors are operated in series under different conditions. Generally, in the two-stage DCL process, coal is dissolved /liquefied, with or without catalyst, in the first stage reactor prior to being hydrocracked and hydro-treated with high activity catalysts in the second stage [11, 12]. It has been widely believed that two-step DCL is superior to single step DCL since higher conversions and oil yields could be obtained with two-step processes [13].

The liquid products from the DCL process consist mainly of cyclic hydrocarbons, and are rich in the medium naphtha-kerosene fraction, and have a lower sulfur content compared to typical high sulfur crude oil. These liquids can be further refined in the same manner as crude oil to yield distillates with light and heavier cuts [14]. Nevertheless, it should be noted that the quality of the product can vary due to the nature of the coal and the coal liquefaction process employed. Thus, coal derived liquids should be carefully analyzed before further processing.

The DCL process options can be classified into three categories: (1) Pyrolysis, (2) Solvent extraction and (3) Catalytic liquefaction [7]. Generally, the DCL process utilizes at least one of those options and sometimes both solvent extraction and catalytic liquefaction, either as a single-stage or two-stage, are used.

1.2.1 Pyrolysis

Coal pyrolysis involves a large number of chemical reactions, which result in the generation of gas, liquid, tar and char (coke) by the thermal decomposition of coal in the absence of oxygen at temperatures in excess of 400 °C (could be as high as 600 °C) under pressures less than 7 bar (generally between 0.3 to 1.6 bar). Pyrolysis, or carbonization, is considered the oldest CTL technique. Although the process is relatively simple, its major disadvantage is that it yields char as the main product and only small amounts of liquid and gas [7].

The product yield of pyrolysis is strongly affected by the coal type and operating conditions, e.g. reaction temperature, pressure and residence time. Figure 4 shows the basic fundamental mechanism that has been reported in many studies [15].

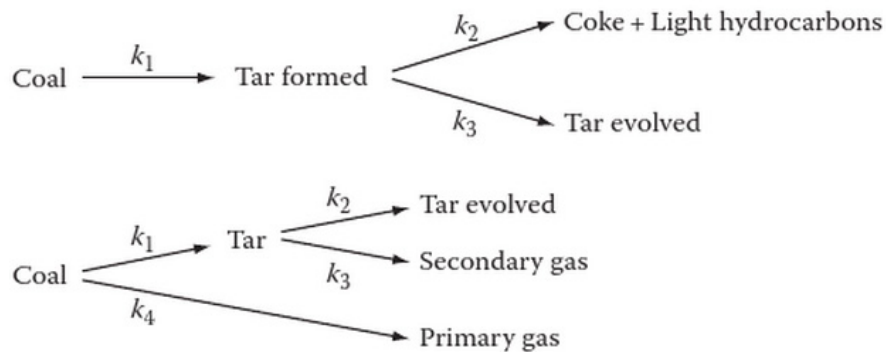


Figure 4: Hypothetical reaction schemes for coal decomposition [15]

Details of the pyrolysis process as well as the liquefaction processes can be found elsewhere [7, 15, 16].

1.2.2 Solvent extraction

Solvent extraction utilizes a hydrogen donor solvent, which is a solvent capable of donating hydrogen to coal molecules under reaction conditions. The process is typically carried out at temperatures up to 510 °C and pressures up to 345 bar. If carried out at mild conditions, the yield of light oil and gas would increase. The yield of liquid product from this process is greater compared to that of the pyrolysis process [7]. Details of the solvent extraction processes can be found elsewhere [16].

It should be noted that solvent extraction, apart from being used in coal liquefaction, has also been used in coal research for isolation and characterization of soluble and insoluble coal fractions in the following areas: (1) extraction yield and selectivity improvement, (2) correlation of solvent swelling and extraction behavior with the structural models representing the insoluble organic portion of coal, and (3) analysis of extract to identify and quantify the organic

compounds in coal and coal-derived products [17]. Solvent extraction has also been pursued for analyzing molecular properties and structure of coal. The solvents used in this process are classified into four groups: (1) non-specific solvents, (2) specific solvents, (3) degrading solvents and (4) reactive solvents [17, 18].

Non-specific solvents (e.g., benzene, hexane, carbon tetrachloride and ethanol), which extract minor portions of coal under mild conditions at temperatures below 100 °C. While in specific solvents (e.g., pyridine, quinolone and n-methyl pyrrolidone) the solubility of the coal material increases to about 20-40%, at temperatures up to 200 °C [17, 18]. Degrading solvents can be fully recovered and could extract up to 90% of coal at temperatures close to their thermal decomposition (up to 400 °C). Mild thermal degradation of coal generally produces smaller soluble fragments. Reactive solvents, which are hydrogen donors, dissolve the coal by chemical interaction. In this process, coal is broken down into fragments by thermal degradation and those fragments are stabilized by hydrogen donated by the solvent, thus producing a product which differs greatly from the original coal. It should be noted that operational or mechanistic distinctions between extraction by degrading solvents and reactive solvents are unclear [18].

1.2.3 Catalytic liquefaction

In catalytic liquefaction, the catalyst facilitates the injection of hydrogen atoms into the coal. The catalyst is typically dispersed throughout the reactor using a liquid solvent, which acts as a heat-transfer medium and provides another route for hydrogen transfer. Older generations of catalysts used in coal liquefaction evolved from catalysts used by hydro-processing in petroleum refineries, which have proved to be capable of performing hydro-treatment on coal-liquid

systems, but with limitations. The reaction conditions for catalytic coal liquefaction range from 400 to 500 °C and 68.9 to 690 bar.

In order to improve the catalytic liquefaction process, two approaches were investigated. The first approach was to develop a better catalysts which are suitable for coal-liquid upgrading, e.g., using a dispersed rather than supported catalysts which have an intimate contact with the surface of coal particles. The second approach was to produce better coal-liquid products (from the dissolution step) which are more amenable to upgrading by conventional catalysts. The latter approach can be achieved through developing a better process for dissolution as well as better catalysts [19]. It is evident that the development of high performance catalysts is the key to the successful development of DCL processes. Unfortunately, severe catalyst deactivation and difficulties associated with catalysts separation from coal liquids remains a major challenge hindering the successful development of the catalytic liquefaction process [19].

So far, several DCL processes have failed to be commercialized; however, the interest in developing DCL technology remains strong because DCL enjoys the following key benefits which are considered advantageous when compared to ICC:

- (1) DCL process produces a larger variety of products and yields less CO₂ at a higher energy efficiency when compared to ICL [11-13].
- (2) With proper hydro-processing, DCL products could yield higher quality, lower sulfur liquids that can be used as transportation fuels and chemical feedstock [11, 12, 14].
- (3) Development of DCL processes offers the opportunity to improve plant economy and operational flexibility via a hybrid (DCL/ICL) design [12].

Despite these advantages, DCL remains at the development stage. The performance of DCL processes can be greatly enhanced with successful development of novel processes which employ improved catalysts and solvents, while operating at mild conditions leading to enhanced efficiency and economic gain. Nonetheless, one of the most important developments in DCL is the Shenhua direct coal liquefaction demonstration plant [20]; other examples can be found elsewhere [11, 12, 16].

1.2.4 Liquefaction using alkali/alcohol

Liquefaction using alkali/alcohol provides a promising prospect for the future of DCL, which through the use of alkali and alcohol (as supercritical solvents), could offer high efficiency processes operating at low temperatures. The advantages of liquefaction using alkali/alcohol include high conversion and product yield [1, 21]. Biomass, e.g., lignin, can also be used as feed to the process [22, 23]; hence, enabling co-liquefaction of coal and biomass, which synergizes the overall process, leading to the moderation of reaction conditions and enhancing the quality as well as the yield of the liquid products[13]. This process is detailed in the following section.

2.0 LIQUEFACTION USING ALKALI/ALCOHOL BACKGROUND

Literature studies have shown that the coal dissolution/liquefaction yield can be increased, if coal or biomass were treated with alkali-alcohol solutions under different operating conditions as shown in Table 1 [21, 22, 24-32]. These studies showed that the reactions generate small products which are structurally similar to the original coal, with overall higher hydrogen and lower oxygen contents [30, 31]. These important results were the main drive behind the development of a novel coal liquefaction process since the products can be subsequently upgraded via hydro-treatment to yield synthetic fuel.

The coal reaction with alkali and alcohol yields pre-asphaltenes, asphaltenes and a small amount of oil. The increased solubility in subsequent solvent extractions [21, 33] indicates that the coal molecules are broken down into smaller ones. Terms such as dissolution, liquefaction and de-polymerization have been used interchangeably by investigators.

Several studies have provided insight on reaction mechanisms [26, 30, 31, 34], conceptual processes [1, 22, 35], as well as effect of reaction conditions on product yield [21, 24-32].

Table 1: Literature studies on coal liquefaction using alkali/alcohol

Feed		Operating condition							Reference [#]
Coal	Weight (g)	Temperature (°C)	Initial Pressure (bar)	Time (h)	Alkali		Solvent		
					Name	Weight (g)	Name	Weight (g)	
Taiheiyo coal	6	350 to 400	Not reported	1	NaOH KOH Ca(OH) ₂ Na ₂ CO ₃	0.15 mol	Methanol Ethanol	30	[24]
Teshio, Taiheiyo Sumiyoshi Akabira, New Yubari Indian Ridge	1 to 6	180 to 450	Not reported	1 to 20	NaOH	1 to 6	Ethanol	10 to 30	[25]
Taiheiyo coal	1	260 to 400	1 bar N ₂	1 to 22	NaOH	1	Ethanol	10	[26]
Teshio, Taiheiyo Sumiyoshi Akabira, New Yubari Indian Ridge	5	300 to 350	1 bar N ₂	5	NaOH	5	Ethanol	50	[27]
Taiheiyo coal	1	300 to 450	1 to 80 bar N ₂ or H ₂	1	NaOH	1	Ethanol	7.9 (10 ml)	[28]

Table 1 (continued)

Feed		Operating condition							Reference [#]
Coal	Weight (g)	Temperature (°C)	Initial Pressure (bar)	Time (h)	Alkali		Solvent		
					Name	Weight (g)	Name	Weight (g)	
Taiheiyo coal	8	290	1 bar N ₂	1	NaOH	8	Methanol Ethanol, Propanol iso-Propanol Butanol iso-Butanol tert-Butanol Pentanol iso-pentanol	80	[29]
Illinois No. 6 coal	5	335	Not reported	1.5	KOH iso- PrOK tert- BuOK	5 to 10 mol	iso-Propanol	75 to 150	[30]
Illinois No. 6 coal	5 to 10	335 to 400	Not reported	0.5 to 1.5	KOH	0.15 mol	Methanol	47.4 (60 ml)	[31]
Wyodak, Wyoming coal (treated with mild HT)	1	200 to 275	69 to 103 bar N ₂	1 to 3	KOH NaOH	3 to 10 wt. % solution in alcohol	Methanol Ethanol iso-PrOH	10 ml alkali- alcohol solution	[1]
Shengli coal	1	300	1 bar N ₂	1	NaOH	0 to 1	Methanol	0 to 7.9 (10 ml/g)	[21]
Cerrejon coal Amagá coal (treated with acid)	1	350 to 440	40 to 100 bar N ₂ or H ₂	1	ZnCl ₂	0.5	Ethanol	8	[36]

Table 1 (continued)

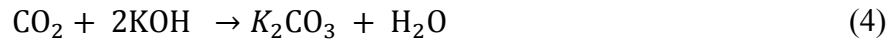
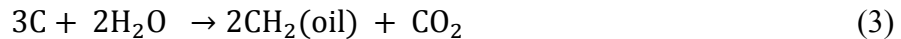
Feed		Operating condition							Reference [#]
Coal	Weight (g)	Temperature (°C)	Initial Pressure (bar)	Time (h)	Alkali		Solvent		
					Name	Weight (g)	Name	Weight (g)	
Lignin and Model compounds	0.434	250 to 290	not reported	0 to 1	NaOH KOH Ca(OH) ₂ Na ₂ CO ₃ CsOH LiOH	10% (w/w) solution in solvent	Methanol Ethanol	4.4 ml solvent	[32]
Lignin	*	270 to 290	not reported	30 s to 15 min	NaOH KOH Ca(OH) ₂ CsOH	0.5 to 1	Methanol Ethanol	1 to 10	[22]
Kraft lignin	1	270 to 315	Not reported	LHSV of 1.4 to 4 h ⁻¹	NaOH	0.5	Water	9.5	[23]

* Methanol/lignin and ethanol/lignin = 1/1 and 10/1

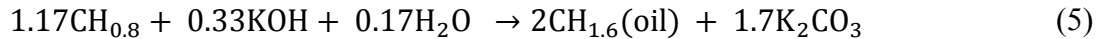
2.1 REACTION MECHANISM

The reaction mechanism could not be fully defined due to the complexity of coal structures. Several studies proposed reaction mechanisms which involve hydrolysis as the main reaction with partial hydrogenation by hydrogen produced from the reaction between alkali and alcohol [24-29]. In the two proposed mechanism shown below, alkali and alcohol are represented by KOH and methanol.

1. Coal hydrolysis with chemical activation by KOH [34]:

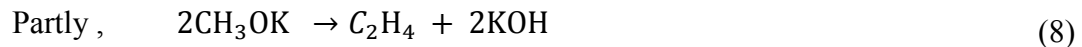
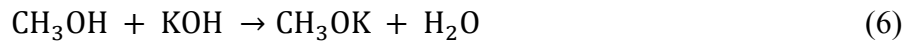


The overall reaction can be written as [34]:



2. Coal methanolysis with methanol, and hydrogenation with hydrogen supplied by the reaction between methanol and KOH [24, 25, 30]:

Also, side reactions that result in hydrogen generation:



2.2 CONCEPTUAL LIQUEFACTION PROCESS USING ALKALI/ALCOHOL

The reactions between coal, alkali and alcohol could lead to the development of a conceptual process for direct coal liquefaction. The reactions can be carried out in a reactor, similar to the solvent extraction steps in the conventional DCL process. In general, the liquefaction reaction is carried out at lower reaction temperatures using alkali and alcohol under supercritical conditions. Therefore, when compared with the conventional DCL process, this type of liquefaction process is less energy intensive and coal extraction in the presence of supercritical fluids often provides better yields.

One example of a conceptual liquefaction process which has been developed consists of 8 steps as shown in Figure 5:

Step 1: Coal pre-extraction with THF. This step is to remove oxygen-containing compounds from coal;

Step 2: Mixing the extracted coal with $ZnCl_2$ or $FeCl_3$ catalyst;

Step 3: Mild hydrotreatment of the extracted coal with catalyst using hydrogen;

Step 4: Catalyst removal and product collection;

Step 5: Base-catalyzed de-polymerization (BCD) of the product from Step 4 using alkali and alcohol under its supercritical conditions;

Step 6: Alkali removal from the BCD products. The product is washed with water and neutralized using HCl.

Step 7: Alcohol removal by drying the product; and

Step 8: Hydro-treatment of the alkali-free product to yield liquid fuel [1].

It should be mentioned that Shabtai et al. [22] previously proposed a similar concept to liquefy biomass products, such as lignin.

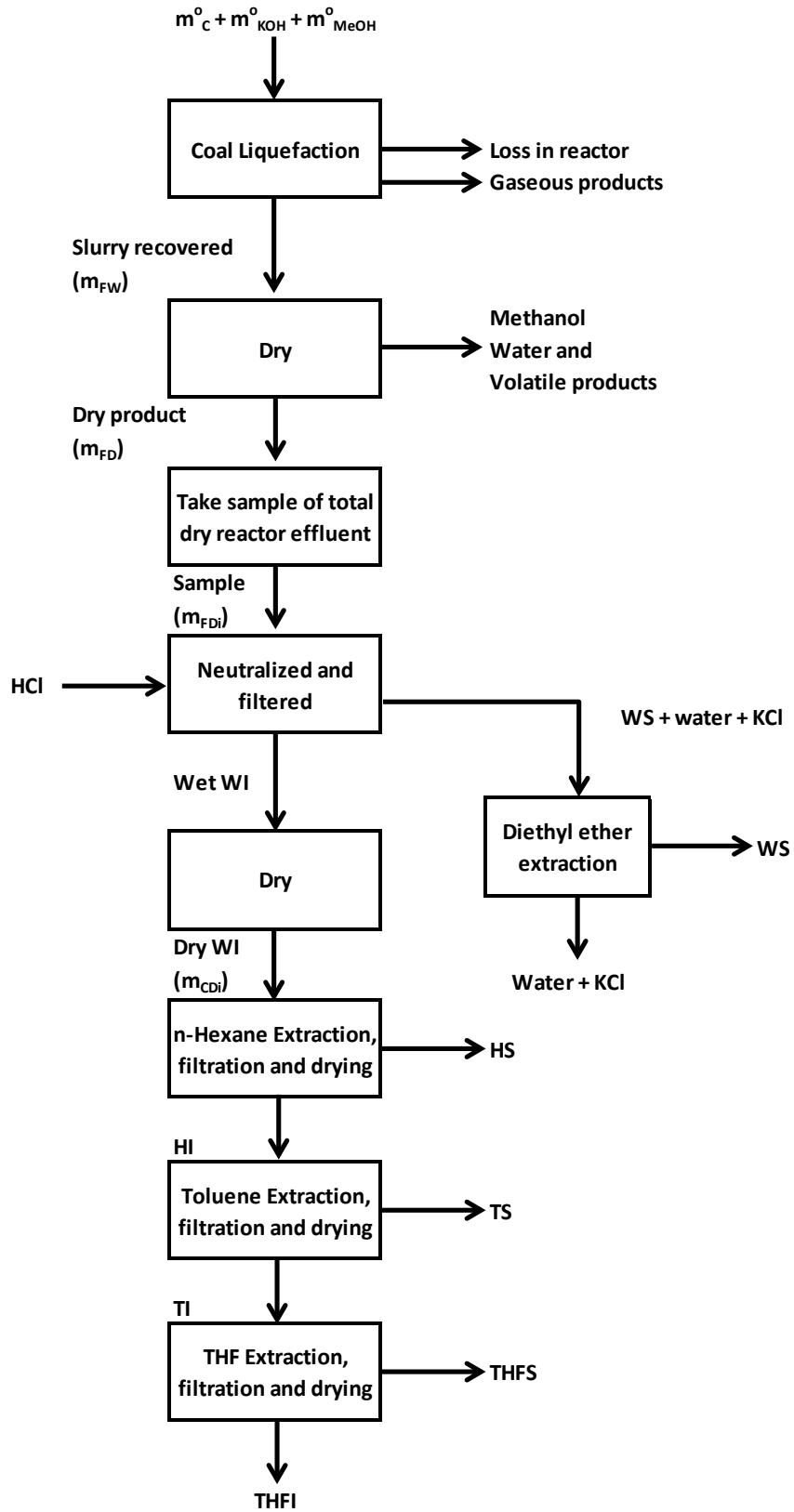


Figure 5: The coal liquefaction process proposed by Shabtai and Saito [1]

Alternatively, liquefaction using alkali/alcohol could be achieved via two-step liquefaction where reactions between coal, alkali and methanol are carried out in the first stage reactor. Then, in the second stage, coal liquid is upgraded via hydro-treatment by the addition of hydro-treating catalyst and hydrogen, similar to the conventional two-stage coal liquefaction process. Suggestions have been made that the products from the first stage should be fed directly into subsequent coal-liquid upgrading steps, thus eliminating the need for filtration, re-heating and re-pressurization units in between, which improves the process economics [35]. Moreover, removing the filtration stage will allow effluents from the first step reaction to react further in the second step reaction resulting in higher yields. The liquefaction process using alkali/alcohol could be simplified using the block diagram depicted in Figure 6.

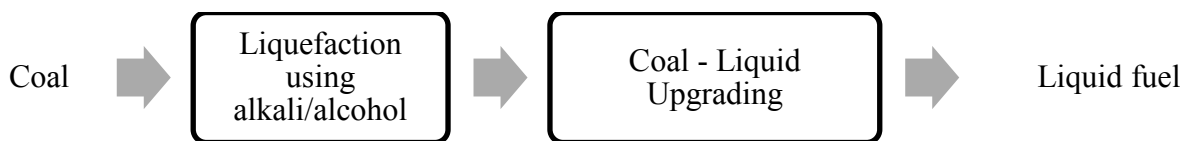


Figure 6: Process block diagram for coal liquefaction using alkali/alcohol

2.3 EFFECT OF REACTION CONDITIONS

The reaction is affected by various parameters, such as temperature, initial pressure, reaction pressure, presence of gases (N₂ and H₂), coal:alkali:alcohol ratio, reaction time, heating rate, coal rank, coal moisture content, type of alcohol and type of alkali used. The effect of each of those parameters is summarized in Table 2.

Table 2: Effect of reaction parameters on the coal liquefaction process

Parameter	Effects
Temperature	The liquefaction yield increased with increasing temperatures. In many cases, the yield reached a maximum at a certain temperature, depending on the other operating conditions, beyond which any further increase in temperature would lead to a decrease in the yield [28, 33].
Reaction pressure	The effect of the actual reaction pressure has not been reported. The effect of pressure was studied as the initial pressure prior to heating.
Initial N ₂ and H ₂ pressure	Higher initial pressure gave higher extract yield [28, 33]. Coal liquefaction under H ₂ atmosphere showed higher extraction yields than those in N ₂ [28]. The extraction yield also increased with increasing pressure for both N ₂ and H ₂ .
Coal rank (C%)	Product yields decreased as the carbon percentage of coal increased [25, 33].
Type of alcohol	Methanol was observed to be the superior choice of alcohol over ethanol and iso-propyl alcohol [1].
Ratio of alcohol: coal	Increasing the alcohol: coal ratio has a slight effect on the product yield and conversion.[21]. Some studies indicated that hydrolysis can occur in the absence of methanol[37].
Type of alkali	There are conflicting reports regarding the effect of the alkali species used. In one report [24], KOH and NaOH resulted in similar product yields . On the other hand, another report revealed that the KOH product yield was significantly greater than that of NaOH [1].
Alkali:coal ratio	Increasing the amount of alkali increased the product yield and conversion [21, 25].
Reaction time	Study results indicated that the product yield reached a maximum at a reaction time of 1 hour before starting to level-off [26, 33].
Coal moisture content	Moisture was found to have a negligible effect on the liquefaction reaction of lignite [21].

As can be seen in this table, the results show some contradictions and the optimum operating conditions have not yet been determined. Future studies should focus on the effects of temperature, coal:alkali:alcohol ratio and coal, alkali and alcohol types used. Moreover, detailed studies should focus on the reaction of coal with KOH and methanol within the temperature range of 280 to 300 °C. This is because KOH and methanol might have the potential to provide the highest yield and conversion when compared to other alkalis and alcohols. In addition, high liquefaction yield and conversion would not be achieved at lower temperatures.

3.0 OBJECTIVE

The objective of this study is to determine the optimum operating conditions, primarily the temperature and reagent:coal ratio, for a non-catalytic direct coal liquefaction process employing KOH/methanol, using two subbituminous coals, namely Rosebud and Wyodak-Anderson. Samples for both coals were obtained from the Penn State Coal Sample Bank and Database. Rosebud coal is from Rosebud seam, Rosebud County, Montana, USA and Wyodak-Anderson coal is from Wyodak seam, Campbell County, Wyoming, USA.

In order to achieve this objective, the yields of direct liquefaction process for each coal were measured over the temperature range from 280 to 300 °C using coal:KOH:methanol ratios of 2:1:9, 2:3:9 and 3:3:9. The optimum operating conditions were defined as those which would provide the greatest products yield using the sequential selective solvent extraction technique.

4.0 EXPERIMENTAL

The experiment consists of two parts; non-catalytic direct liquefaction process using KOH/methanol and products analysis. The direct liquefaction process was carried out batch-wise in a one-liter, high-pressure, high-temperature agitated autoclave. The liquefaction products were analyzed using the sequential selective extraction technique. Details of the experimental setup, operating variables and experimental procedure are given in this section.

4.1 EXPERIMENTAL SETUP

4.1.1 Non-Catalytic Direct Coal Liquefaction Process using KOH/Methanol

The direct coal liquefaction process using KOH/methanol was carried out in a one-liter, high-pressure, high-temperature agitated reactor manufactured by Autoclave Engineers, Inc. The experimental setup, schematically depicted in Figure 7, consists of the following main units:

1. Reactor
2. Monitoring and data acquisition system

4.1.1.1 Reactor

A one-liter agitated reactor manufactured by Autoclave Engineers, Inc. with an effective volume of 1.028 liters was used in this study. The reactor is rated for a maximum working pressure of 376 bar (5450 psi) at a maximum temperature of 454 °C (850 °F). Details and dimensions of the reactor are given in Figure 7 and in Table 3. The reactor is equipped with four baffles located symmetrically to avoid the formation of vortices, an internal cooling coil, an external heating jacket and thermal insulation wrapped around the upper part of the reactor to achieve better temperature control. A hollow shaft connected to a 6 flat-blade impeller is used for mixing. Four holes of 2.4 mm diameter drilled at each end of the hollow shaft enable the reactor to be operated in a gas-inducing mode. The agitator is driven by a magnetic drive with enough capacity to avoid any eccentricity. Two thermocouples [K-type], one for the liquid and the other for the gas phase, and a pressure transducer [custom gage type, part number MMG5.0KV5B4D0T3A5] were used to measure the change of pressure and temperature and transmit the signal to the monitoring and data acquisition system.

4.1.1.2 Monitoring and data acquisition system

The pressure transducers and thermocouples are connected to a personal computer (PC) via the National Instruments' I/O interface. LabView software was used for online data acquisition and monitoring.

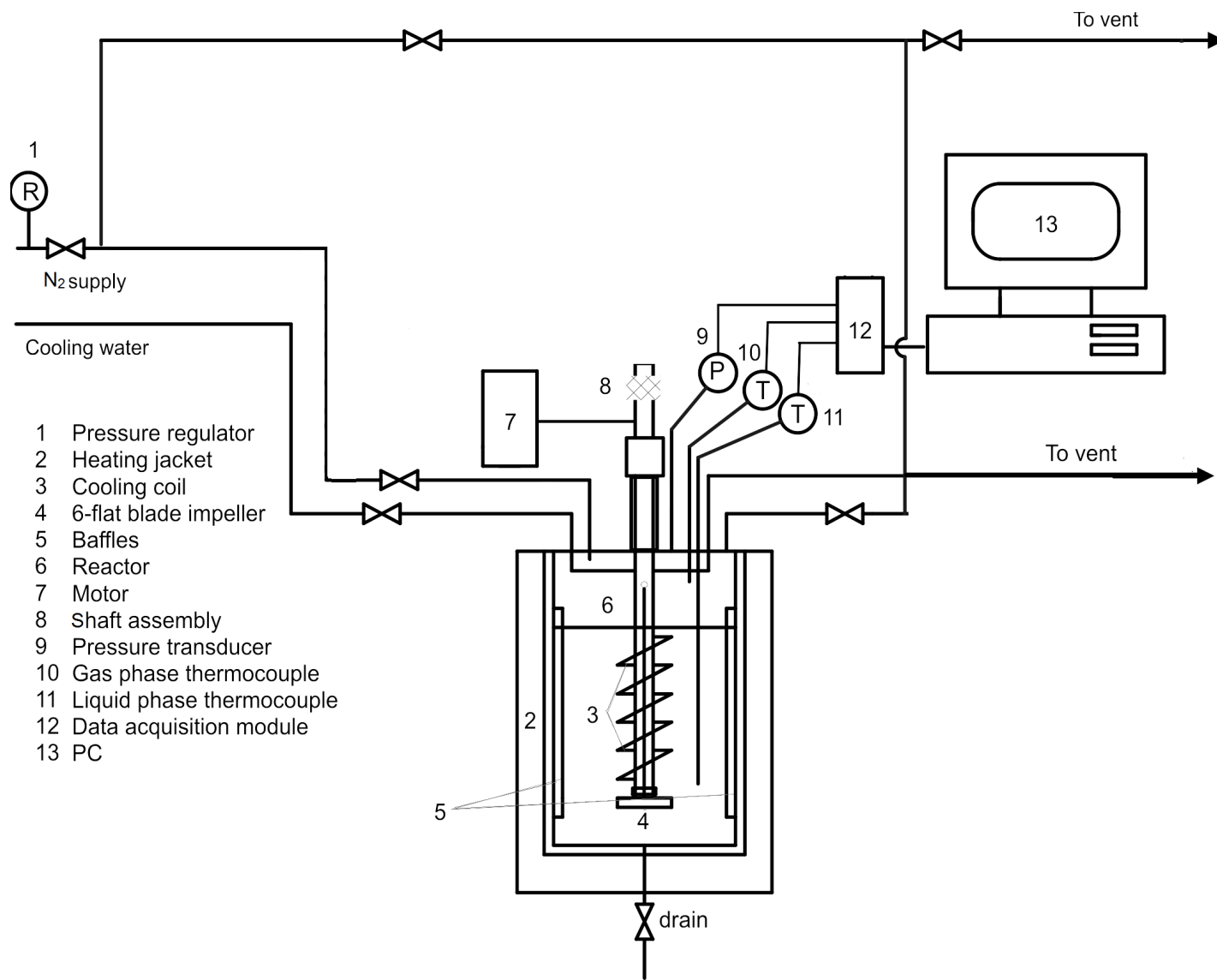


Figure 7: Experimental setup for the coal liquefaction process

Table 3: Reactor Dimensions

Reactor inside diameter, d_T	76
Reactor outer diameter	111
Impeller diameter	31.75
Baffle width ($1/10$ of , d_T)	7.6
Numbers of Baffles	2-4
Reactor material of construction	316 SS
Geometry	Cylindrical
Lower impeller clearance from the bottom	45
Hollow shaft length	178
Number of impeller	1
Number of blades	6
Impeller type	Flat blade disk turbine
Shaft hole diameter	2.4
Reactor inside depth	238
Reactor volume	1.028 liter

Note: all dimensions are in mm unless stated otherwise

4.1.2 Sequential selective solvent extraction technique

The sequential selective extraction technique adopted by Shabtai and Saito[1] and Lei et al. [1, 21] was used for characterization of the coal and coal-derived products. This technique provides a means to compare the performance of different coal liquefaction processes. This is often conducted using specific solvents which are known to extract certain materials in coal, and the coal extracts can then be used to assess the process performance.

The effects of temperature and reagent:coal ratio on the yield of Rosebud and Wyodak-Anderson coals liquefaction process was studied by performing solvent extractions in sequence as shown in Figure 8. The neutralized coal liquefaction products were extracted with n-hexane. The insoluble portion remaining from the n-hexane extraction was subsequently extracted using toluene. Similarly, the toluene insoluble portion was extracted using tetrahydrofuran (THF).

The amounts of soluble products which were produced from the coal, KOH and methanol reactions can be determined from the amounts of product extracted in, water solubles (WS), n-hexane solubles (HS), toluene solubles (TS) and THF solubles (THFS) [1, 21]. The water solubles (WS) were subsequently extracted by using diethylether.

Lei et al. [21] found that each type of solvent extracted certain types of materials by analyzing HS, TS and THFS using FTIR; and the solubles extracted by each type of solvents are given in Table 4.

Table 4: Solubles extracted by different solvents

Solvent	Soluble products
Diethylether	Aliphatic compounds [17]
n-Hexane	Oil (aliphatic compounds) [21]
Toluene	Poly-aromatic and heterocyclic compounds [21]
THF	Phenolic and etheric asphaltenes [21]

The extraction was conducted by mixing the sample with solvent while heating at near its boiling point, and subsequently separating the sample from the solvent used in the analysis [26]. Alternatively, a Soxhlet extractor was used in the extraction process [1, 21].

In this study, the products of the direct liquefaction process were mixed with the solvent in a flask, which was continuously stirred and heated. The solvent extraction was carried out in an apparatus which consists of a round bottom flask, a condenser, an oil-bath and a magnetic stirrer. The samples and solvents were placed in the round-bottom flask connected to the condenser. The round-bottom flask was submerged into the oil-bath as shown in Figure 9.

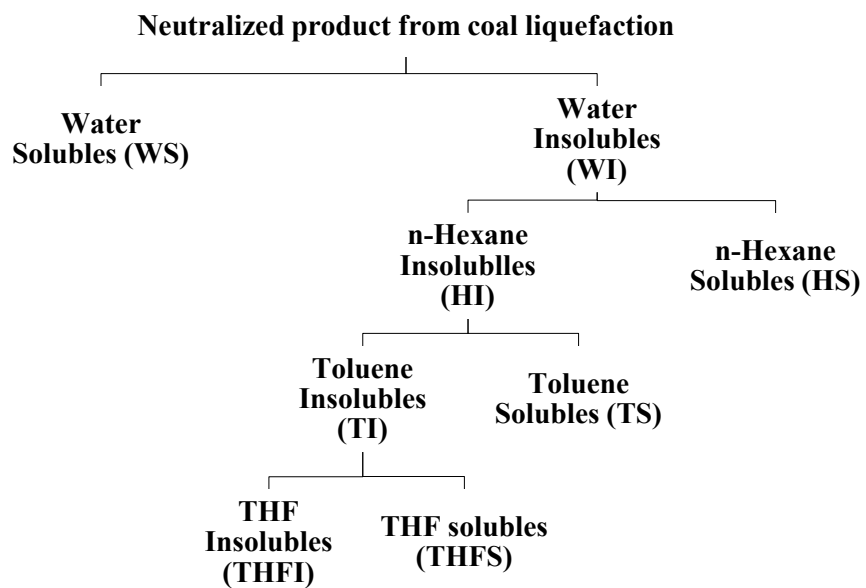


Figure 8: Extraction scheme for the neutralized coal liquefaction product



Figure 9: Photo of the solvent extraction apparatus used

Due to the destructive nature of the analysis, only one batch of the product samples was selected to represent experiments performed under identical conditions. The rest of the samples were stored for future use. 18 representative samples out of 81 collected were analyzed. Two sequential selective solvent extractions of the original unreacted coals were conducted to serve as a reference. In total, 20 samples were used in the extraction experiments.

4.2 OPERATING VARIABLES

4.2.1 Direct coal liquefaction

The direct coal liquefaction process was carried out under the operating conditions given in Table 5. The amounts of chemicals charged into the reactor for each experimental point are given in Tables 6 and 7. For the experiments performed on Rosebud coal, each point was repeated 5 times; whereas, for Wyodak coal, each experimental point was only repeated 4 times.

Table 5: Operating variables for the direct coal liquefaction process

Coals:	Rosebud and Wyodak-Anderson
Pressure:	Initial pressure of 1 bar N ₂
Temperature:	280 to 300 °C
Reaction time:	1 hour
Mixing speed:	1200 rpm
Coal:KOH:methanol ratio	2:1:9, 2:3:9 and 3:3:9 (wt:wt:wt)

Table 6: Amount of chemicals used in Rosebud coal liquefaction experiment

Exp. Point No.	Temperature	Coal	KOH	Methanol
	°C	grams	grams	grams
1	280	60	30	270
2		50	75	225
3		60	60	180
4	290	60	30	270
5		50	75	225
6		60	60	180
7	300	60	30	270
8		50	75	225
9		60	60	180

Table 7: Amount of chemicals used in Wyodak-Anderson coal liquefaction experiment

Exp. Point No.	Temperature	Coal	KOH	Methanol
	°C	grams	grams	grams
10	280	75.0	37.50	337.50
11		62.5	93.75	281.25
12		75.0	75.00	225.00
13	290	75.0	37.50	337.50
14		62.5	93.75	281.25
15		75.0	75.00	225.00
16	300	75.0	37.50	337.50
17		62.5	93.75	281.25
18		75.0	75.00	225.00

4.2.2 Operating conditions of sequential selective solvent extraction

The n-hexane, toluene and THF extractions were performed at 63 °C, 100 °C and 60 °C, respectively, which correspond to approximately 90% of their respective boiling points. All extraction experiments were carried out for 10 hours. Also, filtration and drying after each extraction took 8 and 10 hours, respectively.

4.3 CHEMICALS PROPERTIES

The properties of the chemicals used are described in the following section.

Coal Samples:

Two coal samples from the Penn State coal data bank were used in the experiment:

1. Rosebud Seam (Penn State coal data bank, sample number DECS-10), and
2. Wyodak Seam (Wyodak) (Penn State coal data bank, sample number DECS-26)

Both coals are of the sub-bituminous rank. The nominal size of the coal samples is minus 6 mm.

Their details are given in Appendix A.

The two coals were mined from the Power River Basin region, which according to Kepferle [38], contains the largest reserves of strippable, low ash, and low sulfur coal in the United States. For this reason, both coals could be attractive potential candidates for the development of the direct coal liquefaction process.

The elemental, proximate and ultimate analyses and sulfur content of the coal samples are summarized in Table 8 through 11. The coals were used in the experiments as received without any pre-treatment.

Table 8: Elemental analysis of the coal samples

Basis	Dry Basis		Dry mineral matter free (dmmf)	
	Rosebud	Wyodak	Rosebud	Wyodak
% Carbon	68.12	69.74	79.72	76.29
% Hydrogen	3.54	5.55	4.14	6.07
% Nitrogen	0.92	0.94	1.08	1.03
% Organic sulfur	0.47	0.35	0.55	0.38
% Oxygen	12.40	14.83	14.51	16.23
% Mineral matter	14.55	8.59		
	100.00	100.00	100.00	100.00

Table 9: Proximate analysis of the coal samples

Coal Sample	As received		Dry Basis		Dry ash free (daf)		Dry mineral matter free (dmmf)	
	Rosebud	Wyodak	Rosebud	Wyodak	Rosebud	Wyodak	Rosebud	Wyodak
%Moisture	21.58	26.30	-	-	-	-	-	-
%Ash	9.85	5.58	12.56	7.57	-	-	-	-
%Vol. Matter	32.68	33.06	41.67	44.86	47.66	48.53	46.86	48.13
%Fix Carbon	35.89	35.06	45.77	47.57	52.34	51.47	53.14	51.87

Table 10: Ultimate analysis of the coal samples

Coal	As received		Dry Basis		Dry ash free (daf)		Dry mineral matter free (dmmf)	
	Rosebud	Wyodak	Rosebud	Wyodak	Rosebud	Wyodak	Rosebud (14.20% mm)	Wyodak (8.41% mm)
% Ash	9.85	5.58	12.56	7.57				
% Carbon	53.62	51.42	68.38	69.77	78.19	75.48	79.69	76.18
% Hydrogen	2.89	4.16	3.69	5.64	4.22	6.11	4.3	6.17
% Nitrogen	0.72	0.69	0.92	0.94	1.05	1.01	1.07	1.02
% Total Sulfur	0.91	0.32	1.16	0.43	1.33	0.47	-	-
% Oxygen	10.43	11.53	13.30	15.64	15.21	16.93	14.94	16.63

Table 11: Sulfur contents of the coal samples

Basis	Dry		Dry ash free (daf)	
	Rosebud	Wyodak	Rosebud	Wyodak
% Pyritic	0.68	0.07	0.78	0.08
% Sulfate	0.02	0.01	0.02	0.01
% Organic	0.47	0.35	0.54	0.38
Total	1.17	0.43	1.33	0.47

Other chemicals:

The other chemicals used include methanol, potassium hydroxide, hydrochloric acid, n-hexane, toluene, tetrahydrofuran and diethylether. Some details of the chemicals used are summarized in Table 12.

Table 12: Some details of the chemicals used

Chemicals	Details
Methanol	Methanol was purchased from Fisher Scientific (Product number A412). It is a certified ACS grade with more than 99.8% purity. Boiling point of methanol is 64.7 °C. Its critical point is 240 °C, 78.5 bar
Potassium hydroxide	KOH was purchased from Fisher Scientific in the form of solid pellets (Product number P251). It is FCC/NF grade certified with more than 85% purity.
Hydrochloric acid	Hydrochloric was purchased from J. T. Bakers (Product number 9535-01). Its concentration is 36.5 – 38.0 % v/v.
n-Hexane	n-hexane was purchased from Fisher Scientific (Product number T397-4). Its purity is > 95 wt. %. Boiling point of n-Hexane is 69 °C
Toluene	Toluene was purchased from Fisher Scientific (Product number T324-4). It is a certified ACS reagent grade with >99.5 % purity. Boiling point of Toluene is 110 °C
Tetrahydrofuran	Tetrahydrofuran was purchased from Fisher Scientific (Product number H306-SK4). Boiling point of n-Hexane is 66 °C
Diethyl ether	Diethylether was purchased from Fisher Scientific (Product number AC61507-0040)

4.4 EXPERIMENTAL PROCEDURE

4.4.1 Direct coal liquefaction process using KOH/methanol

The direct coal liquefaction process using KOH/methanol was performed according to the following steps:

1. Coal samples were prepared by splitting and re-mixing several times to ensure that the coal samples were homogenized.
2. Predetermined weights of coal, KOH and methanol were charged into the reactor. The masses of coal, KOH and methanol used for each batch are given in Tables 6 and 7.
3. The reactor was closed and purged with nitrogen and then more N₂ was charged into the reactor to perform a leak test under nitrogen pressure of 35 bar.
4. N₂ was then vented until atmospheric pressure was reached in the reactor.
5. The reactor content was heated to the desired temperature while mixing at 1000 rpm.
6. Once the desired temperature was reached, the mixing speed was increased to 1200 rpm. Mixing was continued at this temperature for 1 hour.
7. After 1 hour, mixing was reduced to 500 rpm and the reactor was cooled by cooling water.
8. Once the ambient temperature is reached, cooling was stopped and the reactor was depressurized.
9. The reactor conditions (pressure, temperature) were recorded from step 5 through 9.
10. The reactor content was collected and stored. The reactor was cleaned before the next experiment (starting at step 2).

4.4.2 Sequential selective solvent extraction technique

The step-by-step procedure of the sequential selective solvent extraction, performed according to the procedure shown in Figure 8, is given below:

1. The reactor content obtained from the direct coal liquefaction process was oven dried in N₂ atmosphere at 100 °C for 24 hours to remove methanol and water.
2. 10 grams sample of the dried reactor content was used in the experiment. The dried coal sample was washed with water and neutralized with HCl in order to remove KOH. The samples were then filtered, yielding a filtrate (water solubles, WS) and retentate (water insolubles, WI).
3. The WI was subjected to n-hexane extraction. 100 grams of n-hexane were used at a temperature of 63 °C for 10 hours.
4. The slurry was then filtered to separate the n-hexane solubles (HS) filtrate from n-hexane insolubles (HI) retentate. The retentate was dried at 100 °C for 10 hours and the weight of dry insolubles was recorded.
5. The solvent extraction procedure described in steps 3 and 4 was repeated using the HI with toluene at temperature of 100 °C for 10 hours.
6. The solvent extraction procedure described in steps 3 and 4 was repeated using TI with THF at temperature of 60 °C for 10 hours.
7. The WS was extracted using diethyl ether which was separated from water using a decanter. Diethyl ether was then vaporized and the weight of the residue was recorded. It should be noted that other investigators [21] used MgSO₄ to remove the remaining moisture, however, in our study, this was not necessary.
8. The extraction procedure was subsequently repeated for all selected samples.

5.0 CALCULATIONS

The calculations performed include pressure prediction of the supercritical methanol in the reactor at different temperatures, in addition to the material balance calculations for each experimental run.

5.1 ESTIMATION OF THE PRESSURE OF SUPERCRITICAL METHANOL

If no reactions were to take place in the reactor, the pressure in the reactor would be attributed to the presence of the supercritical methanol and the moisture content of coal. The pressure of methanol was determined as a function of temperature and density from methanol PVT data at supercritical conditions [39] and the data are shown in Figure 10. The temperature was recorded during the experiment. The density of methanol was determined from the mass of methanol in the reactor and the volume occupied by methanol assuming one-phase. This volume was estimated by subtracting the volume occupied by coal and KOH from the reactor volume.

The partial pressure due to the coal moisture content was negligible according to the calculations conducted using Aspen Properties V7.2 software given in Appendix B.

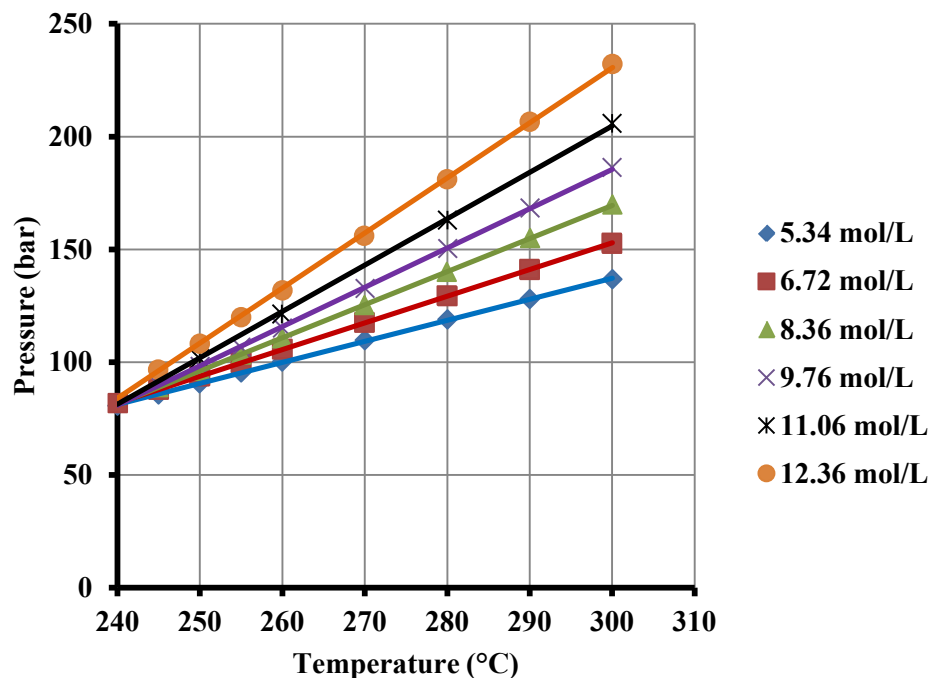


Figure 10: P-T behavior of supercritical methanol at different densities

The coal densities were estimated from ultimate and sulfur analyses of coal [40]. The calculated densities of Rosebud and Wyodak-Anderson coals were 1.541 g/cm^3 and 1.288 g/cm^3 respectively.

5.2 MATERIAL BALANCE CALCULATIONS

A block diagram for material balance calculations in each step of the experiment is given in Figure 11. The volatile and soluble product yield calculations are described in the following section.

5.2.1 Volatile products yield calculation

The volatile components yield was calculated from the mass of the converted coal, which was estimated from the difference between the original mass of coal fed to the reactor and the mass of products collected after drying. For a given run, known mass of coal as received (m_C^o) along with known masses of KOH (m_{KOH}^o) and methanol (m_{MeOH}^o) were put into the reactor. The mass of dry coal feed (m_{DC}^o) was calculated from the mass of coal as received as follows:

$$m_{DC}^o = m_C^o \times (1 - S_{wi}) \quad (9)$$

S_{wi} is the coal moisture content in mass fraction.

After finishing an experiment, the total mass of the wet reactor content was collected (m_{FW}); and then methanol, water and volatile products were removed by drying. The mass of the dry product (m_{FD}) represents the mass of dry coal (m_{DC}) and the mass of KOH (m_{KOH}) as:

$$m_{FD} = m_{DC} + m_{KOH} \quad (10)$$

In each run, a 10-grams sample was taken from m_{FD} and used in the sequential selective solvent extraction. The mass of this sample denoted (m_{FD_i}) was assumed to be representative to the entire mass of m_{FD} and accordingly m_{FD_i} can be written as:

$$m_{FD_i} = m_{DC_i} + m_{KOH_i} \quad (11)$$

The total mass of the sample m_{FD_i} was washed with water and neutralized with HCl in order to remove KOH. The sample was then filtered and dried and the final mass of the dry sample (m_{DC_i}) was recorded.

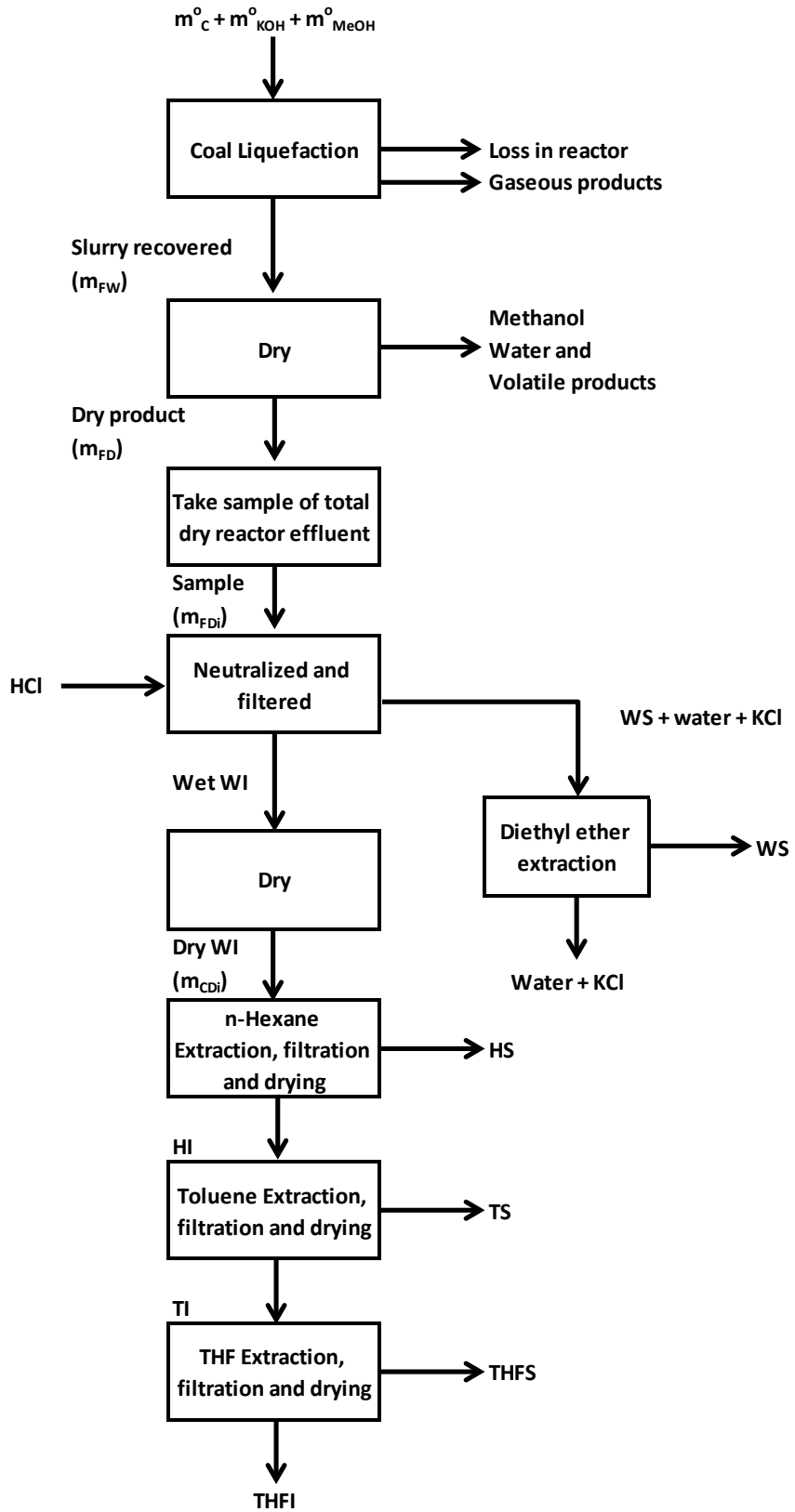


Figure 11: Material balance block diagram

The mass fraction of coal in this sample is defined as:

$$y_{DCi} = \frac{m_{DCi}}{m_{FDi}} \quad (12)$$

Since this sample was assumed to be representative of the total dried coal collected (m_{DC}), the mass of the dry coal in the collected coal was calculated as:

$$m_{DC} = y_{DCi} \times m_{FD} \quad (13)$$

Thus, the yield of the volatile products in coal, which went to the gas-phase, obtained in this experiment was calculated:

$$\text{Yield of the volatile products} = \frac{m_{DC}^o - m_{DC}}{m_{DC}^o} \quad (14)$$

In the above calculations, it was assumed that no coal loss occurred during the experiment; however, it should be mentioned that some of the liquefaction products sticking on the inside wall of the reactor could not be completely removed. This loss was not accounted for in the material balance calculations as it was assumed to be negligible.

Mass of dry coal in the sample (m_{DCi}) was normalized to get mass of dry coal feed in the sample:

$$m_{DCi}^o = \frac{m_{DC}^o}{m_{DC}} \times m_{DCi} \quad (15)$$

5.2.2 Soluble products yield calculation

The total yield of the solubles in the solvent extraction steps, expressed in percentage, was calculated based on dry basis as follows [21]:

$$\text{Total yield of the solubles} = \frac{m_{WS} + m_{HS} + m_{TS} + m_{THFS}}{m_{DCi}^o} \quad (16)$$

Where m_{WS} , m_{HS} , m_{TS} , and m_{THFS} are the mass of solubles in water, n-hexane, toluene, and tetrahydrofuran, respectively; and m_{DCi} is the mass of the coal sample used in the experiment. It should be noted that the mass of water solubles (m_{WS}) obtained by diethyl ether extraction was very small (less than 0.01 g); hence the m_{WS} was neglected. Therefore, Equation **Error! Reference source not found.** can be written as:

$$\text{Total yield of the solubles} = \frac{m_{HS} + m_{TS} + m_{THFS}}{m_{DCi}^o} \quad (17)$$

6.0 RESULTS AND DISCUSSION

The results of the direct coal liquefaction process are discussed based on the pressure data and coal product yields. Each experiment was repeated 4-5 times to insure reproducibility of the experimental data collected. The error and reproducibility of the data is given in Appendix C.

6.1 PRESSURE EXPERIMENTAL DATA

The reactor pressure depends on the temperature, amount of methanol and amount of gaseous volatiles removed from the coal sample or generated during the process. In all experiments, the pressure appeared to increase with temperature during the heating period; and once the desired temperature was reached, the pressure continued to change. This change of pressure could be due to the generation of gaseous products including H₂ and/or vaporization of methanol. This behavior was supported by the behavior of the recorded pressure during and at the end of the experiment. It was systematically observed when the reactor was cooled to ambient temperature that the reactor pressure did not return to its original value at the start of the experiment prior heating.

The maximum pressures reached during the experiments are presented in Figures 12 and 13 for Rosebud and Wyodak-Anderson coal, respectively. As can be seen in these figures, the reactor maximum pressure increased with increasing temperature regardless of the C:K:M ratio,

however, the pressure values corresponding to C:K:M ratio of 2:3:9 are consistently higher than those measured at the other C:K:M ratios.

The effect of increasing KOH on the maximum pressure can be observed by comparing the pressure values corresponding to C:K:M ratio of 2:1:9 with those at 2:3:9 in both figures. As can be concluded, increasing KOH resulted in higher maximum pressure due probably to the generation of more gaseous products including hydrogen in the reactor.

The effect of reagent (methanol + KOH) to coal ratio on the maximum pressure can be concluded by comparing the maximum pressure values corresponding to C:K:M ratio of 2:3:9 with those at 3:3:9 depicted in Figures 12 and 13 for Rosebud and Wyodak-Anderson coals, respectively. As can be observed in these figures, increasing the reagent:coal ratio led to higher maximum pressures for the two coals indicating once again an increase of the gaseous products generated.

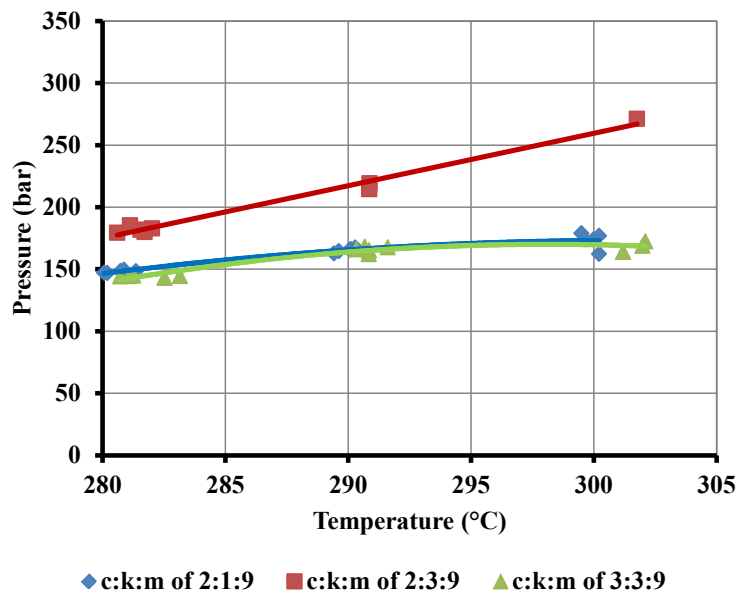


Figure 12: Maximum pressure observed using Rosebud coal

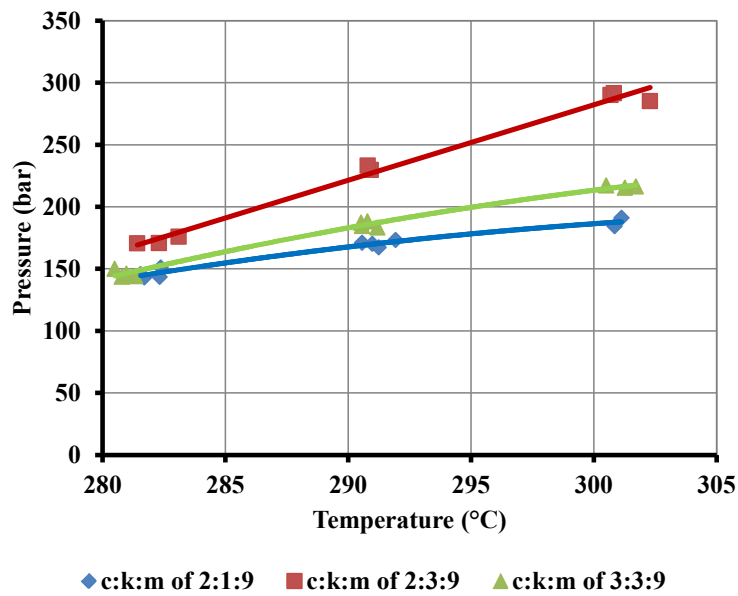


Figure 13: Maximum pressure observed using Wyodak-Anderson coal

The final pressures inside the reactor recorded at ambient temperature are illustrated in Figure 14 and Figure 15 for Rosebud and Wyodak-Anderson coals, respectively. The results confirmed that gaseous products were generated as the result of the liquefaction process. The two figures show that at the same C:K:M ratio of 2:3:9, the pressure corresponding to the gaseous products generated of the Wyodak-Anderson coal increased with increasing temperature, however, the pressure for the Rosebud coal reached a maximum at 290 °C.

The effect of increasing KOH on the final pressure at ambient temperature can be deduced by comparing the measured pressure values corresponding to C:K:M ratio of 2:1:9 with that at 2:3:9 in both figures. As can be observed, increasing KOH resulted in higher final pressure probably due to the generation of more hydrogen and more light gaseous products in the reactor.

The effect of reagent (methanol + KOH) to coal ratio can be seen by comparing the measured final pressure values corresponding to C:K:M ratio of 2:3:9 with that at 3:3:9 in

Figure 14 and Figure 15 for Rosebud and Wyodak-Anderson coals, respectively. As can be observed, increasing the reagent to coal ratio led to higher pressures for the two coals indicating once again an increase of the gaseous products generated. It should be mentioned that even though the gaseous products were not analyzed in this study, Makabe et al. [25] analyzed them and found they include H_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_8 and C_4H_{10} . In the same study with different coal and operating conditions, these authors also found C_5H_{12} .

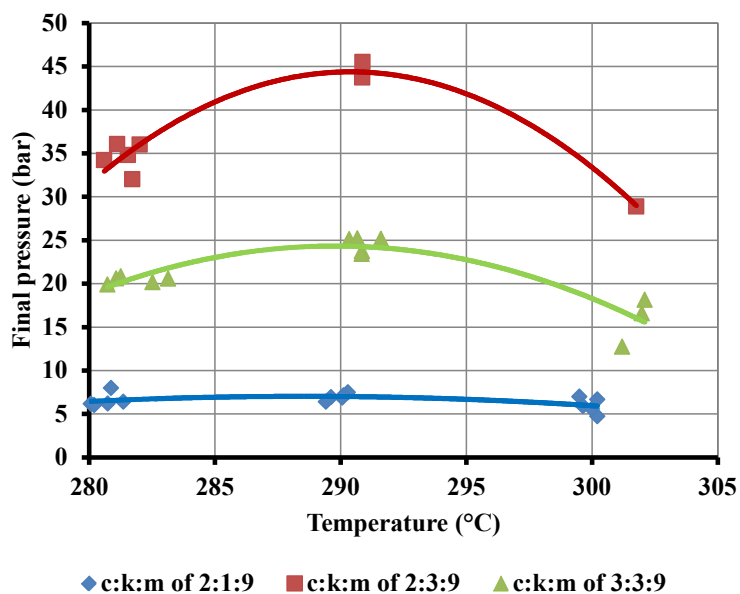


Figure 14: Reactor pressure at ambient temperature (at the end of the run) using Rosebud coal

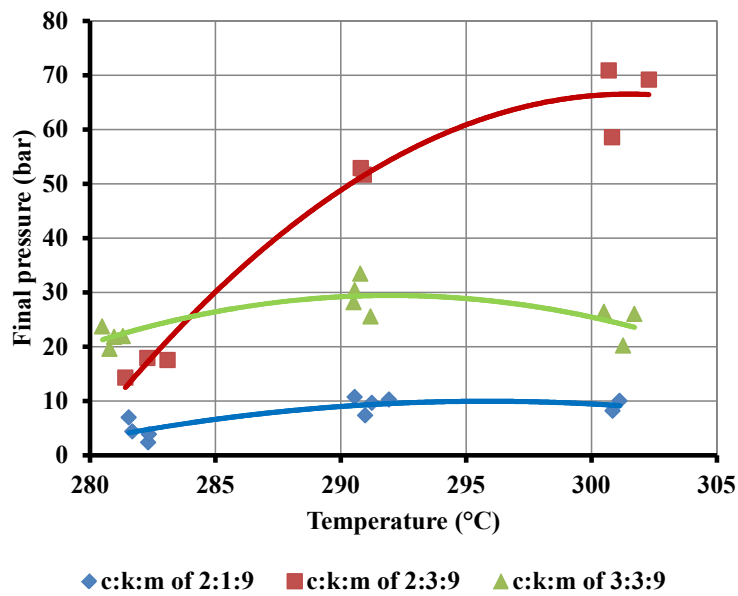


Figure 15: Reactor pressure at ambient temperature (at the end of the run) using Wyodak-Anderson coal

6.2 SEQUENTIAL SELECTIVE SOLVENT EXTRACTION RESULTS

The effects of temperature, amount of KOH and reagent:coal ratio on the yields of the liquefaction process for both the Rosebud and Wyodak-Anderson coals are discussed by comparing the volatile and soluble product yields obtained from the sequential selective solvent extraction process.

Soluble products yield of the original unreacted coals were found to be minimal. Only 1.83 wt% and 2.29 wt% of the total soluble products were recovered from the Rosebud and Wyodak coals. The amount of material extracted from each solvent extraction is, in all cases, lower than 1.2 wt%.

6.2.1 Effect of temperature on the Yields of Rosebud and Wyodak-Anderson coals

6.2.1.1 Effect of temperature on liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 2:1:9

Figure 16 shows the effect of temperature on the liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 2:1:9. For Rosebud coal, the HS yield showed a minimum at 290°C, whereas TS and THFS yields both increased with increasing temperature before leveling off at 300°C. For Wyodak-Anderson coal, there was a significant increase in the TS and volatile products yields with increasing temperature; however, the THFS yield remained almost unchanged at different temperatures.

For Rosebud coal, the volatile products yield also increased with increasing temperature as a result of more coal molecules being broken down at higher temperature. Considering that the pressure at the end of the run changed only slightly with increasing temperature (as shown in Figure 14), the volatile products generated could be made of light hydrocarbon components which were liquid at ambient conditions. For Wyodak-Anderson coal, a marginal increase in the final gas pressure showed a dramatic increase of volatile products with increasing temperature. This led to a conclusion that the volatile products were light liquid which remained in the liquid-phase at ambient conditions.

At this condition, the Rosebud coal always generates better results, giving higher liquid yields compared to those of Wyodak-Anderson coal. The gas product present at the end of the process was considered small indicating that the volatile products were not present in the gas phase. The increase of yields with increasing temperature could be due to the fact that, at 2:1:9 C:K:M ratio, higher temperature promotes the hydrolysis reaction and hydrogenation by the hydrogen generated from the reaction between KOH and methanol.

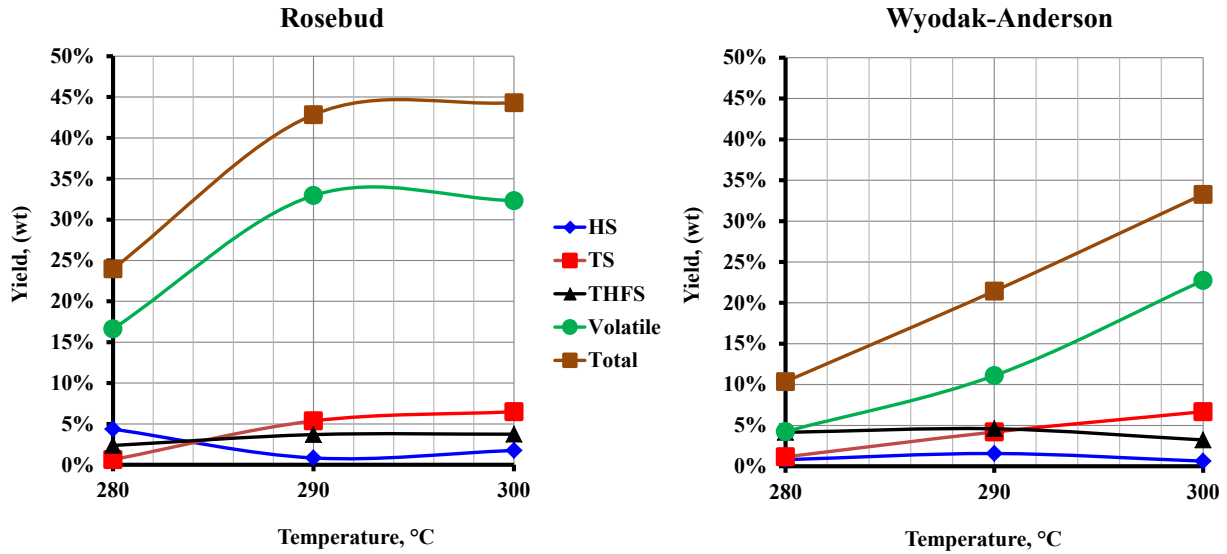


Figure 16: Effect of temperature at on the yields of Rosebud and Wyodak-Anderson coals at 2:1:9 C:K:M ratio

6.2.1.2 Effect of temperature on liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 2:3:9

Figure 17 shows the effect of temperature on the liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 2:3:9. For Rosebud coal, the figure indicates that HS yield at 280 °C was negligible and THFS yield increases with temperature. It should be noted that the TS yields reached a maximum at 290 °C. The soluble products yield increased with temperature before leveling off at 290 °C. For the Wyodak-Anderson coal, on the other hand, the HS yield decreases, while the TS yield increases with increasing temperature. The THFS yield declined as the temperature reached 290 °C before increasing to a maximum at 300 °C.

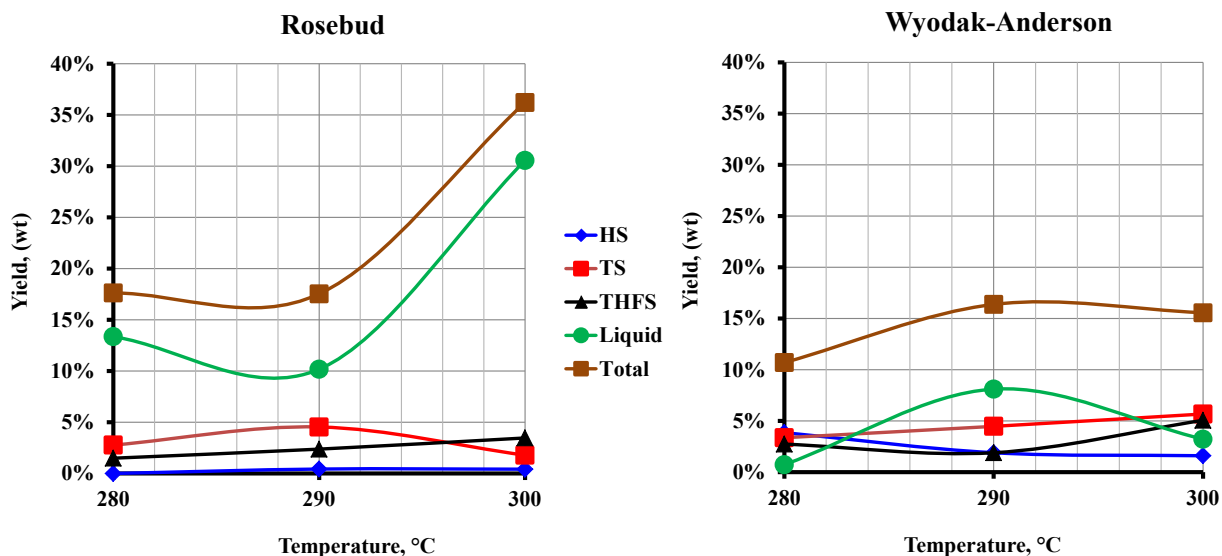


Figure 17: Effect of temperature at on the yields of

Rosebud and Wyodak-Anderson coals at 2:3:9 C:K:M ratio

Figure 17 also shows that for Rosebud coal, the volatile products yield and total yield decreases to a minimum as temperature increases to 290 °C, then increases sharply with increasing temperature. The pressure data shown in Figure 14 indicate that more gaseous products are present at 290 °C despite minimal volatile product yield. Below 290 °C, the volatile products generated may consist mainly of hydrogen produced by the reaction between KOH and methanol, in addition to some light hydrocarbons, such as CH₄, C₂H₄ and C₂H₆. Above 290 °C, the volatile products yield increased while gas pressure decreased with increasing temperature, indicating that less light hydrocarbon gases were produced as the temperature increased. For the Wyodak-Anderson coal, however, the volatile products yield exhibits the opposite trend; as it reaches a maximum at 290 °C before declining with further increase of temperature. The pressure data shown in Figure 15, which appear to increase with temperature, led to suggest that the light liquid productions were favored at temperature lower than 290 °C. Above 290 °C,

increasing temperature appeared to lower the process yield and the gaseous products generated could be hydrogen and light hydrocarbon gases.

6.2.1.3 Effect of temperature on liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 3:3:9

Figure 18 shows the effect of temperature on the liquefaction yields for Rosebud and Wyodak-Anderson coals at C:K:M ratio of 3:3:9. For Rosebud coal, the figure shows that the HS and total yields decrease with increasing temperature, while the TS yield reaches a maximum at 290 °C and the THFS yield decreases slightly with increasing temperature. Also, as the temperature increases above 280 °C, the total yield appears to sharply decrease. It should be mentioned that for Wyodak-Anderson coal, the HS and TS yields also exhibit minimum values at 290 °C.

Figure 18 also illustrates that the light products yield and total yield of the Rosebud coal increase to a maximum as the temperature increases from 280 to 290 °C then decrease sharply as the temperature increases above 290 °C. The pressure data shown in Figure 14 appear to exhibit a similar trend. It seems that the volatile products were evenly distributed between light gases and light liquids. For Wyodak-Anderson coal, the THFS, volatile products and total yields, on the contrary, appear to reach a maximum at 290 °C. Also, the pressure data shown in Figure 15 display the same trend as the volatile products; thus, the volatile products could be made of light liquids and some light gases.

At this condition, the amount of gases at the end of the run increased with increasing temperature, leading to a decrease of the total product yields. Therefore, it can be inferred that much of hydrogen generated was not consumed by free-radicals during the reaction. The retrogressive reactions, e.g., cross-linking by the decomposition of the oxygen functional groups

and the recombination/re-polymerization of free-radicals, appeared to be getting stronger with increasing temperature [11].

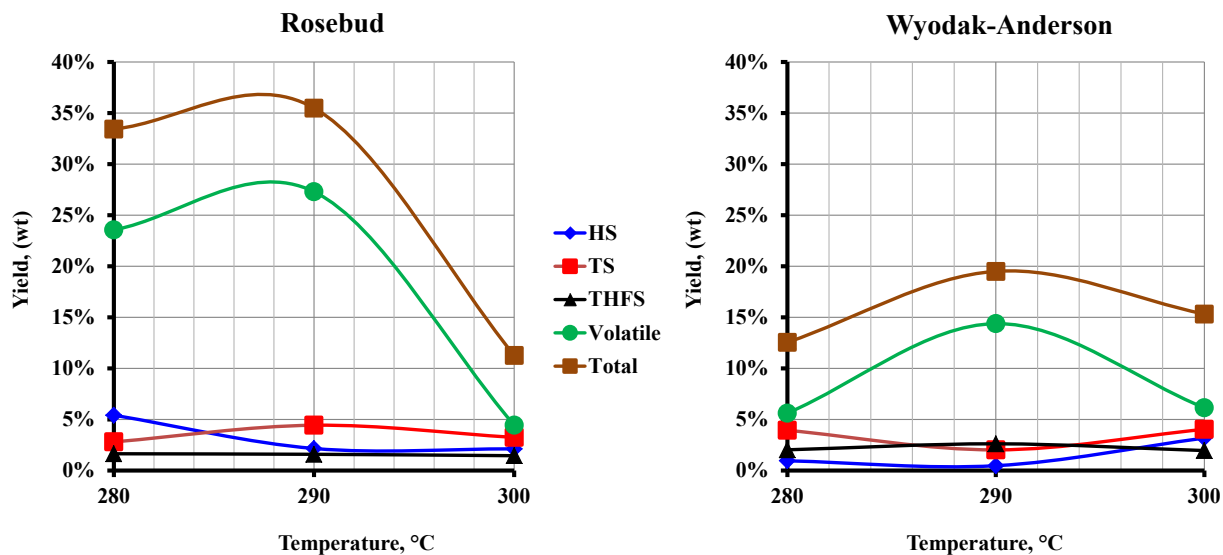


Figure 18: Effect of temperature at on the yields of Rosebud and Wyodak-Anderson coals at 3:3:9 C:K:M ratio

6.2.2 Effect of KOH on the Yields of Rosebud and Wyodak-Anderson coals

6.2.2.1 Effect of KOH on the Yields of Rosebud and Wyodak-Anderson coals at 280 °C

Figure 19 shows the effect of KOH on the liquefaction yields for Rosebud and Wyodak-Anderson coals at 280 °C. At C:K:M ratio of 2:1:9, Rosebud coal gives higher HS, THFS and volatile products yields than those at C:K:M ratio of 2:3:9. On the other hand, at C:K:M ratio of 2:1:9, the gas pressure was lower than that at C:K:M ratio of 2:3:9 as shown in Figure 14. Therefore, adding more KOH to Rosebud coal at 280°C reduced the total yield and increased the yield of gaseous products.

Figure 19 also shows that for Wyodak-Anderson coal, HS and TS yields increase with increasing KOH. Also, the yield of gaseous products at C:K:M ratio of 2:3:9 ratio was greater than that at C:K:M ratio of 2:1:9. It seems that increasing KOH resulted in high yield of light gaseous products including hydrogen and a slightly high total liquid yield.

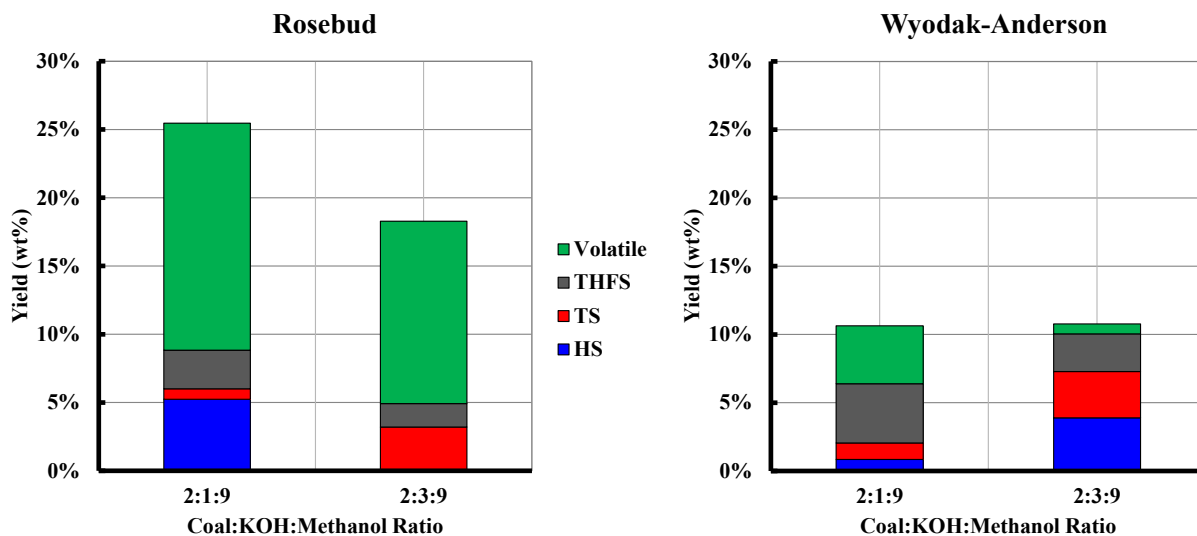


Figure 19: Effect of KOH on the yields of Rosebud and Wyodak-Anderson coals at 280 °C

6.2.2.2 Effect of KOH on the Yields of Rosebud and Wyodak-Anderson coals at 290 °C

Figure 20 shows the effect of KOH on the direct liquefaction yields for Rosebud and Wyodak-Anderson coals at 290 °C. As can be seen in this figure for Rosebud coal, higher HS, TS, THFS and volatile product yields are obtained at C:K:M ratio of 2:1:9 when compare with those obtained at C:K:M ratio of 2:3:9. Therefore, increasing KOH resulted in lower total yield and higher gaseous products yield for Rosebud coal as shown Figure 14.

For Wyodak-Anderson coal (shown in Figure 20), increasing the C:K:M ratio from 2:1:9 to 2:3:9 decreases THFS and volatile products yields, while HS and TS yields slightly increase.

Accordingly, increasing KOH led to lower total liquid yield, but higher gaseous products for Wyodak-Anderson coal.

Thus, for both coals used at 290 and 300 °C, increasing KOH decreased the total liquid yield and increased the gaseous products yield. This could be due to the reaction between KOH and methanol to form hydrogen which went to the gas-phase, leading ultimately to low coal conversion. It should be mentioned that under similar operating conditions, Rosebud coal performed better than Wyodak-Anderson coal as it gave greater total product yields.

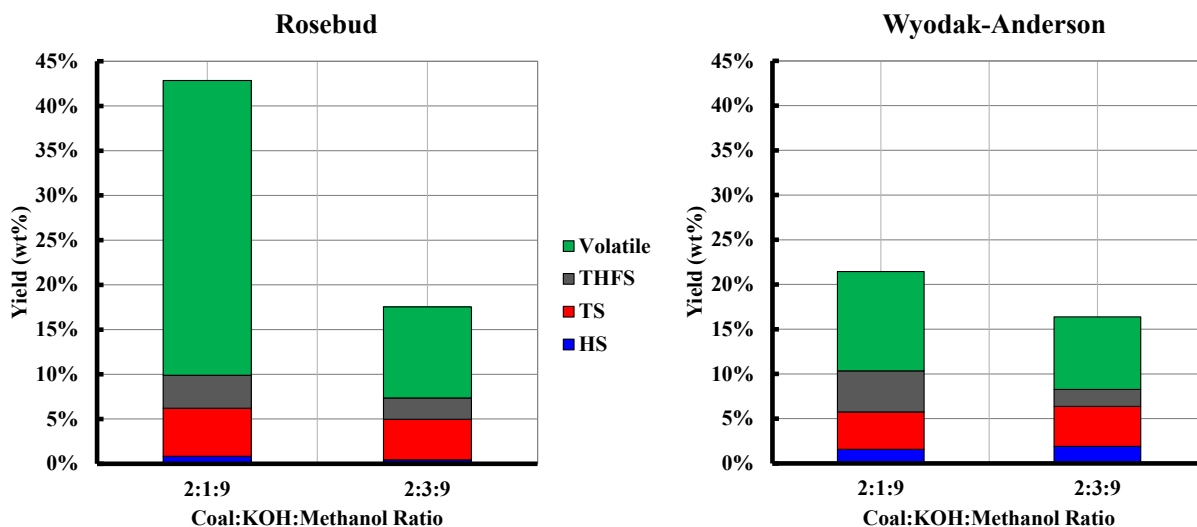


Figure 20: Effect of KOH on the yields of Rosebud and Wyodak-Anderson coals at 290 °C

6.2.2.3 Effect of KOH on the Yields of Rosebud and Wyodak-Anderson coals at 300 °C

Figure 21 shows the effect of KOH on the direct liquefaction yields for Rosebud and Wyodak-Anderson coals at 300 °C. For Rosebud coal, HS, TS, THFS and volatile products yields appear to decrease with increasing KOH. At this temperature, the gas pressure at C:K:M ratio of 2:1:9 is greater than that at 2:3:9 as depicted in Figure 14. As for Wyodak-Anderson coal, HS and

THFS appear to increase, whereas TS and total liquid yield decrease with increasing KOH.

Figure 15 also shows the gas pressure increased with increasing KOH.

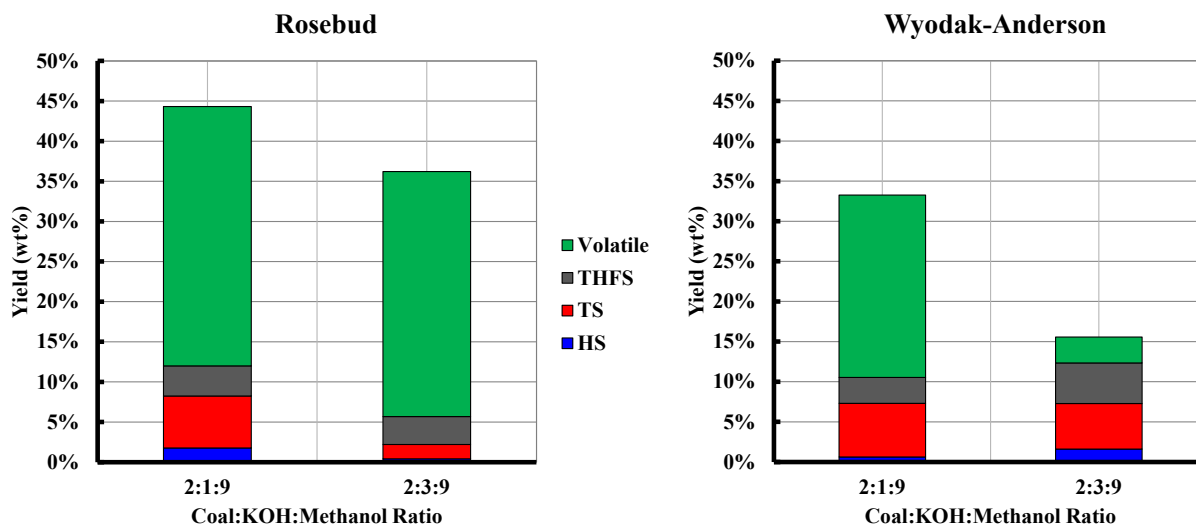


Figure 21: Effect of KOH on the yields of Rosebud and Wyodak-Anderson coals at 300 °C

6.2.2.4 Remarks on the effect of KOH on the Yields of both coals

For Rosebud coal, our results indicated that increasing the KOH resulted in lower total yields and higher gas pressure at the three temperatures used. These results supported the assumption that the gas present at the end of the run consisted mainly of hydrogen and light gases (possibly CH_4 , C_2H_4 and C_2H_6) that were generated from the reaction between KOH and methanol. If the gas present at the end of the run were volatile products, the volatile products yield should have increased with increasing the reactor pressure. These results appear to contradict those by Lei et al. [21] who claimed that increasing NaOH increased the total yield. However, this could be because lignite, which were used in their study, respond to the reaction with NaOH and methanol in a different manner. In our case, it can be inferred that, for sub-bituminous coal,

there is an optimum value of KOH at which further increase would lower total yield in favor of hydrogen and light gases production.

For Wyodak-Anderson coal, our data indicated that increasing KOH led to an increase of the gas pressure and a decrease of the volatile products yield at all temperature used. At 280 °C, increasing KOH slightly increase the liquid yield. At 290 and 300 °C, however, increasing KOH decreased the total yield and increased the light gaseous products yield.

7.0 CONCLUDING REMARKS

- The addition of methanol and potassium hydroxide (KOH) to coal at high temperatures from 280 to 300 °C appeared to dissolve/liquefy portions of Rosebud and Wyodak-Anderson coals to produce hydrogen, light and liquid hydrocarbon products. The experimental data obtained using the sequential selective solvent extraction technique showed that the liquid products yield can be as high as 44.3%. The effect of temperature on the yields of the direct liquefaction process was dependent on coal type and the coal:KOH:methanol ratios used.
- The gaseous products at the end of each run consisted of light hydrocarbons and hydrogen gas which were generated due to the reactions among KOH, methanol and coal. Portion of the hydrocarbon products might be present in the gas-phase; however, the majority remained in the liquid-phase at ambient conditions as indicated by material balance calculations.
- The presence of potassium hydroxide appeared to favor hydrogen production over liquid hydrocarbons production, leading to a high yield of gaseous products and low total yield of liquid hydrocarbon products.
- The highest yield of liquid products was obtained at 300 °C and C:K:M ratio of 2:1:9 for both coals used. At this condition, Rosebud coal gave higher liquid products yield when compared with those of Wyodak-Anderson coal. The reason for this behavior could be

attributed to the fact that the mineral content in Rosebud coal is twice that in Wyodak-Anderson coal, since minerals could have catalytic activities.

- Based on the results obtained in his study, the Rosebud coal is a better choice as a feedstock for the direct coal liquefaction process, as it provided the highest yield at a C:K:M ratio of 2:1:9 and 300 °C. Rosebud coal, however, did not always give more favorable results when compared with those of Wyodak-Anderson coal under the other operating conditions used.
- It should be emphasized that the liquefaction product yields obtained in this study were much lower than those by Shabtai and Saito [1] and Lei et al. [21], who reported liquefaction yields up to 90%. The reasons for such a behavior can be attributed to the following: (1) the coals used in this study were not subjected to pretreatment (e.g., THF pre-extraction and mild hydrotreatment) nor to subsequent catalytic hydrotreatment; (2) the subbituminous coals used in this study are less effective in liquefaction using KOH/methanol when compared with low rank coals [21], such as Lignite; and (3) the extraction of the products by filtration followed by sequential selective solvent extraction used in this study might be less accurate than using a Soxhlet extractor.

8.0 FUTURE WORK

In their base-catalyzed coal liquefaction process, Shabtai and Saito [1] reported product yields nearing 90%. In this study, the maximum yield obtained was 44.3% at 300 °C with Rosebud coal. The reason for Shabtai and Saito's higher yields could be attributed to the fact that they preconditioned and hydrotreated the coal using $ZnCl_2$ or $FeCl_3$ catalyst before the base-catalyzed liquefaction process as well as applying hydrotreatment using sulfide CoMo catalyst after the base-catalyzed liquefaction. Thus, a logical future extension to this study would be to use catalyst and hydrogen with the remaining coal samples collected and kept in our laboratory for future utilization. This is because the coal liquefaction yields was reported to be strongly dependent on the type of solvents, extraction temperature, extraction time as well as preconditioning and hydrotreatment [17]. Also, extraction of the coal liquefaction product yields could be enhanced using a Soxhlet.

APPENDIX A

DETAILS OF COAL FROM PENN STATE COAL SAMPLE BANK AND DATABASE

Details of coal were reproduced from the original database received from Penn state.

Rosebud Seam
Rosebud County, MT

printed 5/22/98
sampled 6/13/90

SAMPLE LOCATION

Rosebud County, Montana, USA
Near Colstrip, Montana
Northern Great Plains Coal Province
Fort Union Region

Colstrip SW (7.5') Topographic Quadrangle
Latitude 45°48'29" North, Longitude 106°39'30" West

SAMPLE HISTORY

Working Section Channel Sample collected Jun 13, 1990 by Penn State
Mining method: surface
6" high pyrite coal below pit floor not sampled
Coal Sample Bank reserve: 164 kg (361 lbs)

SAMPLE HISTORY

Paleocene

Fort Union Formation
Seam thickness at sample location: 676 cm (22 ft 2 in.)
Sample thickness: 569 cm (18 ft 8 in.)

PROXIMATE ANALYSIS	<u>as rec'd</u>	<u>dry</u>	<u>daf</u>	<u>dmmf(Parr)</u>
%Moisture	21.58			
%Ash	9.85	12.56		
%Vol. Matter	32.68	41.67	47.66	46.86
%Fix Carbon	35.89	45.77	52.34	53.14

SULFUR FORMS	<u>dry</u>	<u>daf</u>
%Pyritic	0.68	0.78
%Sulfate	0.02	0.02
%Organic	0.47	0.54
%Total	1.17	1.33

Moisture
% as received 21.58
% equilibrium 23.98

ULTIMATE ANALYSIS	<u>as rec'd</u>	<u>dry</u>	<u>daf</u>	<u>dmmf (Parr)</u>
%Ash	9.85	12.56		(14.20%MM)
%Carbon	53.62	68.38	78.19	79.69
%Hydrogen	2.89*	3.69	4.22	4.3
%Nitrogen	0.72	0.92	1.05	1.07
%Total Sulfur	0.91	1.16	1.33	
%Oxygen (diff.)	10.43*	13.30	15.21	14.94

* excluding H and O in moisture
Dry % Chlorine = 0.07 Dry % Carbon Dioxide = 0.91

ELEMENTAL ANALYSIS	<u>dry</u>	<u>dmmf (Mod.P)</u>
		(14.55% MM)
% Carbon	68.12	79.72
% Hydrogen	3.54	4.14
% Nitrogen	0.92	1.08
% Organic sulfur	0.47	0.55
% Oxygen	12.40	14.51
% Mineral matter	14.55	

CALORIFIC VALUE (GROSS)	<u>dry</u>		<u>As rec'd moist</u>		<u>Equil. moist</u>	
	<u>MJ/kg</u>	<u>Btu/lb</u>	<u>MJ/kg</u>	<u>Btu/lb</u>	<u>MJ/kg</u>	<u>Btu/lb</u>
MM-containing	26.831	11536	21.042	9047	20.398	8770
MM-free (Parr)	31.115	13378	23.558	10129	22.751	9782
MM-free (Mod. Parr)	31.299	13457	23.675	10179	22.861	9829
Net, dmmf Btu/lb	30.368	13057				

Mott-Spooner different = 294 Btu/lb

ATOMIC RATIOS (dmmf)	<u>Parr</u>	<u>mod. Parr</u>
Atomic H/C	0.648	0.622
Atomic O/C	0.141	0.134

RANK CALCULATIONS

ASTM Rank (equilibrium moist.)	subB
(as rec'd moist.)	subB

MACERAL COMPOSITION (blue + white light, volume %)

	Mineral-free
Textinite	0.0
Ulminite	34.8
Humodetrinite	37.4
Gelinite	0.6
Corpohuminite	0.7
Total Huminite	73.5
Fusinite	
Semifusinite	
Macrinite	
Micrinite	
Sclerotinite	
Inertodetrinite	
Total Inertinite	16.4
Sporinite	2.4
Resinite	0.4
Alginite	0.0
Suberitnite	0.0
Cutinite	0.0
Liptodetrinite	7.2
Exudatinite	0.1
Bituminite	0.0
Fluorinite	0.0
Total Liptinite	10.1

REFLECTANCE DATA

Huminite:	Mean-max R _O : 0.42%	
<u>Vtypes:</u>	<u>V 3</u>	<u>V 4</u>
Percent:	30.0	20.0

CAKING AND MECHANICAL PROPERTIES

		<u>Gieseler Coal Plastometer:</u>	
Free-swelling index	0	Initial softening	n.d.
		Maximum fluidity	n.d.
Hardgrove grindability index	45.5	Solidification	n.d.
Vickers' microhardness index	n.d.	Fluid temp. range	n.d.
Washability data not available		Maximum fluidity	n.d.

Rosebud Seam
Rosebud County, MT

printed 5/22/98
sampled 6/13/90

INORGANIC ELEMENT ANALYSIS

	<u>Major Elements</u>		<u>Trace Elements</u>		
	Oxide % of HTA		Element % of whole dry coal	Ppm HTA	Ppm whole dry coal
SiO ₂	37.0	Si	2.3	Ag	
Al ₂ O ₃	17.9	Al	1.3	As	
TiO ₂	0.76	Ti	0.06	Ba	6628
Fe ₂ O ₃	9.14	Fe	0.85	Be	4.0
MgO	3.31	Mg	0.26	Bi	
CaO	13.2	Ca	1.3	Cd	
Na ₂ O	1.17	Na	0.12	Ce	
K ₂ O	0.48	K	0.05	Cl	
P ₂ O ₅	0.31	P	0.020	Co	
SO ₃	16.2			Cr	50
				Cu	70
				Ga	
				Ge	
				Hg	
				La	
				Mn	1162
				Nb	
				Ni	
				Pb	
				Rb	25
				Sc	
				Se	
				Sn	
				Sr	4059
				Th	
				U	
				V	15
				Y	
				Yb	
				Zn	35
				Zr	290

High-temperature ash (HTA)
used for in organic analysis
= 13.26 % of whole dry coal

ASH FUSION TEMPERATURESReducing atmosphereOxidizing atmosphere

Initial deformation	1138 °C	2080 °F	1204 °C	2200 °F
Softening	1179 °C	2155 °F	1238 °C	2260 °F
Hemispherical	1204 °C	2200 °F	1260 °C	2300 °F
Fluid	1232 °C	2250 °F	1285 °C	2345 °F

Wyodak Seam (Wyodak-Anderson)
Campbell County, WY

printed 5/22/98
sampled 6/09/94

SAMPLE LOCATION

Campbell County, Wyoming, USA
Near Wright, Wyoming
Northern Great Plains Coal Province
Fort Union Region

Reno Reservoir (7.5') Topographic Quadrangle
Latitude 43° 40'00" North, Longitude 105°15'00" West

SAMPLE HISTORY

Run-of-mine Sample collected June 9, 1994 by Penn State
Mining method: surface
Sampled from 38 cuts of automatic sampler

Coal Sample Bank reserve: 278 kg (613 lbs)

SAMPLE HISTORY

Paleocene
Fort Union Formation
Seam thickness at sample location: 2134 cm (70 ft 0 in.)

PROXIMATE ANALYSIS	<u>as rec'd</u>	<u>dry</u>	<u>daf</u>	<u>dmmf(Parr)</u>
%Moisture	26.30			
%Ash	5.58	7.57		
%Vol. Matter	33.06	44.86	48.53	48.13
%Fix Carbon	35.06	47.57	51.47	51.87

SULFUR FORMS	<u>dry</u>	<u>daf</u>
%Pyritic	0.07	0.08
%Sulfate	0.01	0.01
%Organic	0.35	0.38
%Total	0.43	0.47

Moisture
% as received 26.30
% equilibrium 26.23

ULTIMATE ANALYSIS	<u>as rec'd</u>	<u>dry</u>	<u>daf</u>	<u>dmmf (Parr)</u>
%Ash	5.58	7.57		(8.41%MM)
%Carbon	51.42	69.77	75.48	76.18
%Hydrogen	4.16*	5.65	6.11	6.17
%Nitrogen	0.69	0.94	1.02	1.03
%Total Sulfur	0.32	0.43	0.47	
%Oxygen (diff.)	11.538	15.64	16.92	16.63

* excluding H and O in moisture
Dry % Chlorine = 0.0 Dry % Carbon Dioxide = 0.12

ELEMENTAL ANALYSIS	<u>dry</u>	<u>dmmf (Mod.P)</u> (8.59%MM)
% Carbon	69.74	76.29
% Hydrogen	5.55	6.07
% Nitrogen	0.94	1.03
% Organic sulfur	0.35	0.38
% Oxygen	14.83	16.23
% Mineral matter (incl. 0.13% FeS ₂)	8.59	

CALORIFIC VALUE (GROSS)	<u>Dry</u>		<u>As rec'd moist</u>		<u>Equil. moist</u>	
	<u>MJ/kg</u>	<u>Btu/lb</u>	<u>MJ/kg</u>	<u>Btu/lb</u>	<u>MJ/kg</u>	<u>Btu/lb</u>
MM-containing	28.247	12145	20.819	8951	20.837	8959
MM-free (Parr)	30.787	13237	22.156	9526	22.177	9535
MM-free (Mod. Parr)	30.892	13282	22.219	9553	22.240	9562
Net, dmmf Btu/lb	29.559	12709				

Mott-Spooner different = -477 Btu/lb

ATOMIC RATIOS (dmmf)	<u>Parr</u>	<u>mod. Parr</u>
Atomic H/C	0.973	0.956
Atomic O/C	0.164	0.160

RANK CALCULATIONS

ASTM Rank (equilibrium moist.)	subB
(as rec'd moist.)	subB

MACERAL COMPOSITION (blue + white light, volume %)

	Mineral-free
Textinite	0.0
Ulminite	41.6
Humodetrinite	41.1
Gelinite	1.1
Corpohuminite	1.9
Total Huminite	85.7
Fusinite	3.3
Semifusinite	3.1
Macrinite	0.3
Micrinite	0.6
Sclerotinite	0.1
Inertodetrinite	2.3
Total Inertinite	9.7
Sporinite	3.6
Resinite	0.4
Alginite	0.0
Suberitnite	0.6
Cutinite	0.0
Liptodetrinite	0.0
Total Liptinite	4.6

REFLECTANCE DATA

Huminite:	Mean-max R _O : 0.29%		
<u>Vtypes:</u>	<u>V 1</u>	<u>V 2</u>	<u>V 3</u>
Percent:	2.0	62.0	36.0

CAKING AND MECHANICAL PROPERTIES

		<u>Gieseler Coal Plastometer:</u>	
Free-swelling index	0	Initial softening	n.d.
		Maximum fluidity	n.d.
Hardgrove grindability index	47.2	Solidification	n.d.
Vickers' microhardness index	n.d.	Fluid temp. range	n.d.
Washability data not available		Maximum fluidity	n.d.

INORGANIC ELEMENT ANALYSIS						
<u>Major Elements</u>				<u>Trace Elements</u>		
	Oxide % of HTA		Element % of whole dry coal		Ppm HTA	Ppm whole dry coal
SiO ₂	31.7	Si	1.00	Ag		< 0.2
Al ₂ O ₃	16.1	Al	0.60	As		1
TiO ₂	1.27	Ti	0.05	Ba	4657	311
Fe ₂ O ₃	4.84	Fe	0.23	Be	< 2.0	< 0.1
MgO	4.64	Mg	0.19	Bi		
CaO	23.5	Ca	1.10	Cd		< 0.2
Na ₂ O	1.8	Na	0.09	Ce		
K ₂ O	0.4	K	0.02	Cl		
P ₂ O ₅	0.89	P	0.026	Co		
SO ₃	12.7			Cr	45	3
				Cu	135	9
				Ga		
				Ge		
				Hg		0.12
				La		
				Mn	155	10
				Nb		
				Ni	35	2
				Pb		
				Rb	10	1
				Sc		
				Se		
				Sn		
				Sr	2452	164
				Th		
				U		
				V	160	11
				Y		
				Yb		
				Zn	85	6
				Zr	245	16

High-temperature ash (HTA)
used for in organic analysis
= 6.68 % of whole dry coal

ASH FUSION TEMPERATURES				
	<u>Reducing atmosphere</u>		<u>Oxidizing atmosphere</u>	
Initial deformation	1149 °C	2100 °F	1185 °C	2165 °F
Softening	1166 °C	2130 °F	1199 °C	2190 °F
Hemispherical	1182 °C	2160 °F	1213 °C	2215 °F
Fluid	1196 °C	2185 °F	1235 °C	2255 °F

APPENDIX B

ASPEN PROPERTIES ANALYSIS

The effect of water presence on the supercritical methanol pressure was investigated using Aspen V7.2 properties analysis. The water-methanol system pressure was generated as a function of mass fraction of water at different temperature as shown in Table 13.

Table 13: Pressure and mass fraction of water in a water-methanol system

Temperature (°C)	Mass fraction of water (fraction)	Pressure (bar)
268.3	0	
268.3	0.8	128.604
268.3	0.6	128.604
268.3	0.4	128.604
268.3	0.2	128.604
268.3	0	128.604
282.2	1	
282.2	0.8	157.3845
282.2	0.6	157.3845
282.2	0.4	157.3845
282.2	0.2	157.3845
282.2	0	157.3845
296.1	1	
296.1	0.8	190.7171
296.1	0.6	190.7171
296.1	0.4	190.7171
296.1	0.2	190.7171
296.1	0	190.7171
310.0	1	
310.0	0.8	229.0041
310.0	0.6	229.0041
310.0	0.4	229.0041
310.0	0.2	229.0041
310.0	0	229.0041

APPENDIX C

REPRODUCIBILITY OF THE EXPERIMENTAL RESULTS

Reproducibility of the experimental results was verified by examining the amount of product recovery, which was defined as mass of the reactor effluent recovered from each experimental batch, and maximum pressure data. The product recovery and pressure data were plotted with Absolute Average Relative Error (AARE) as shown in Figures Figure 22 through Figure 25.

AARE and σ_{AARE} were determined from the following equations:

$$AARE = \frac{1}{N} \sum_i^n \frac{|x_i - \bar{x}|}{\bar{x}} \quad (18)$$

$$\sigma_{AARE} = \sqrt{\sum_i^n \frac{(x_i - AARE)^2}{N - 1}} \quad (19)$$

The calculated AARE values of the fractional product recovery were less than 11.7% with 13.5% standard deviation. The fractional product recovery is defined as the mass of the slurry (coal + KOH + CH₃OH) recovered from the reactor at the end of the experiment divided by the original mass of those components fed to the reactor at the beginning of the experiment.

The calculated AARE values of the pressure data were less than 5.8% with 4.2% standard deviation. It can be concluded that the experimental results are fairly reproducible.

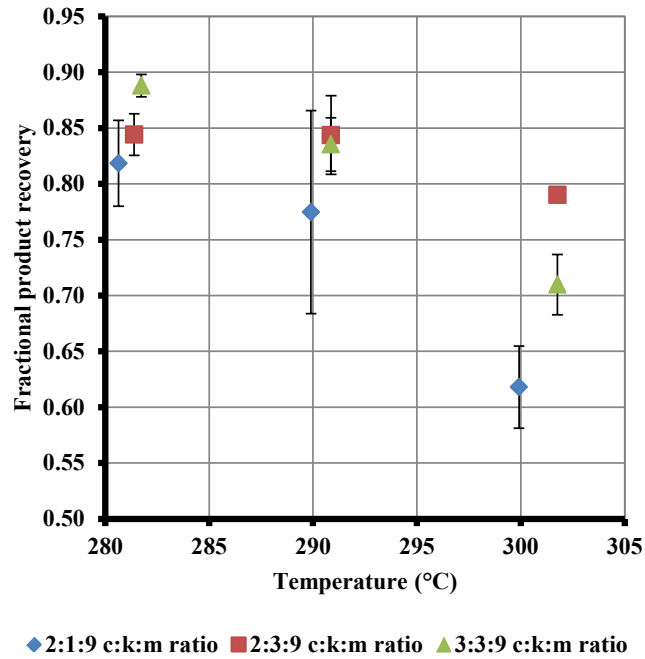


Figure 22: Fractional product recovery and standard error bar for Rosebud coal

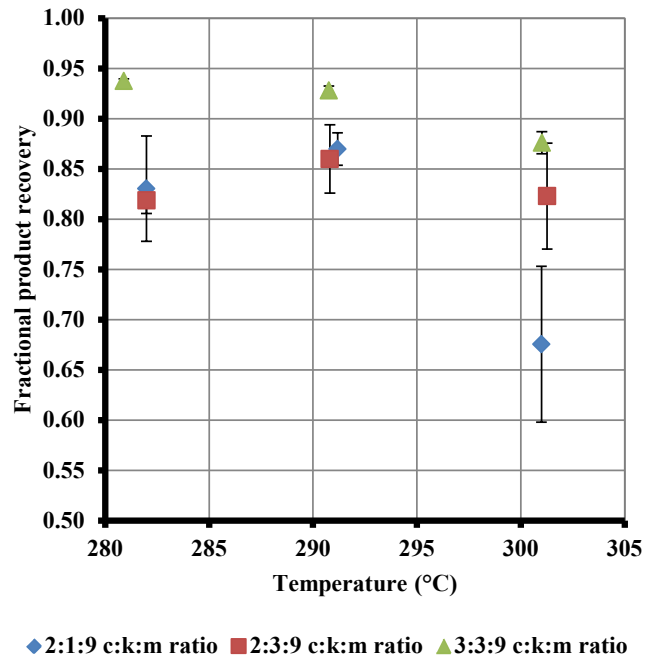


Figure 23: Fractional product recovery and standard error bar for Wyodak-Anderson coal

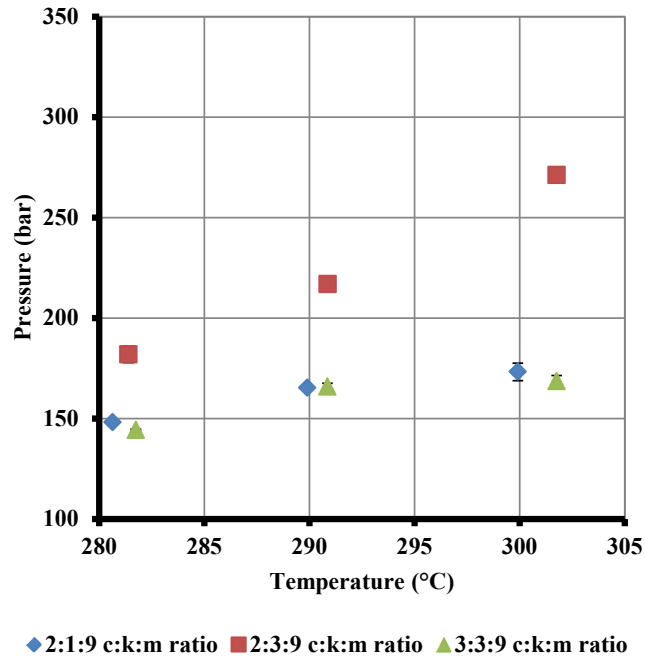


Figure 24: Maximum pressure data and standard error bar for Rosebud coal

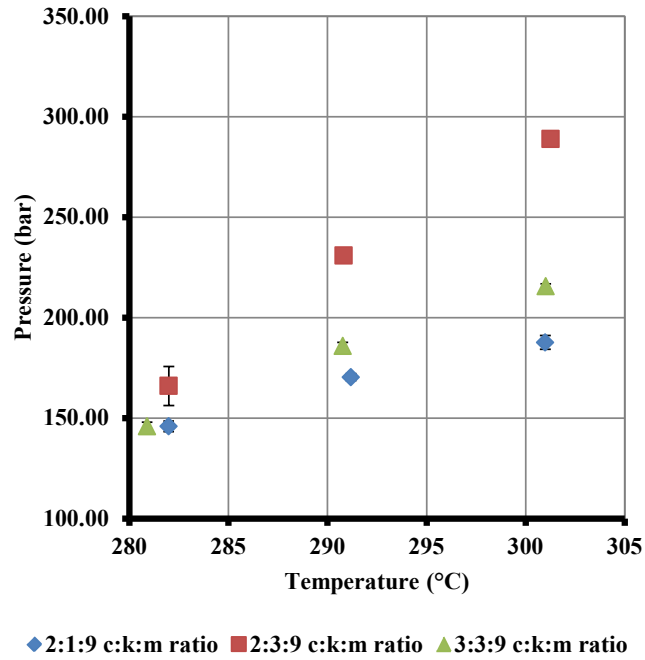


Figure 25: Maximum pressure data and standard error bar for Wyodak-Anderson coal

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