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Fischer-Tropsch Synthesis for Kerosene-Range Products Using a Multi-Component Catalyst Supported on Coal-Based Activated Carbon

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**Fischer-Tropsch Synthesis for Kerosene-Range Products Using a Multi-Component
Catalyst Supported on Coal-Based Activated Carbon**

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Thesis Submitted to the
College of Engineering and Mineral Resources

At West Virginia University

In partial fulfillment of the requirements

for the degree of

Master of Science

In

Chemical Engineering

Advisory Committee

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2011

Keywords: Fischer-Tropsch, Coal-based activated carbon support, Iron-based catalysts

Abstract

Fischer-Tropsch Synthesis for Kerosene-Range Products Using a Multi-Component Catalyst Supported on Coal-Based Activated Carbon

Soumya J. Gujjar

The effect of varying the composition of an iron-based catalyst on the performance of Fischer-Tropsch synthesis was studied. The main focus is towards liquids in the range C₉ through C₁₅ hydrocarbons, the kerosene/gasoline range hydrocarbons sometimes called the single battlefield fuel. The baseline catalyst was 6%Mo, 16%Fe, 0.8%Cu and 0.9%K supported on anthracite activated-carbon support. Catalysts with 0% Mo and 12% Mo loadings, 0%Fe and 32% Fe loadings, 0% Cu and 1.6%Cu loadings, and 0%K and 1.8%K loadings were investigated. The reaction was carried out at a temperature of 300°C, pressure of 300 psig and syngas (H₂/CO ratio = 1) flowrate of 100 sccm/min. Catalysts were characterized by BET, TPR and EDX. The data gathered were also fitted to a regression model.

The FT activity and the CO₂ selectivity increase on increasing Fe loading. A small amount of potassium increases FTS activity, while larger amounts decrease FTS activity. Also, a small amount of Mo results in an increase in FTS activity but the activity decreases on addition of more Mo. Varying the copper loading has very small effects on all parameters.

Dedicated to Mummy and Pappa

Acknowledgement

I would like to express my sincere gratitude for my research advisors, Dr. Dady Dadyburjor and Dr. Edwin Kugler for their guidance and encouragement during the course of this work. I would also like to sincerely thank Dr. John Zondlo for being a part of my research committee and for sharing his knowledge and suggestions.

I would also like to thank the staff members of Chemical Engineering, Mr. Liviu Magean and Ms. Gabriela Perhinschi, Ms. Adrienne McGraw for helping me with catalyst characterization. I am grateful to Linda Rogers and Bonita Helmick for patiently helping me out in all my non-academic but important issues. I would like to thank Dr. Chunchuan Xu and Tristan McQuain for guiding me with preparation of activated carbon support. Also, I would like to thank every graduate student and faculty at the Chemical Engineering department, WVU, for their warmth and for making my stay in Morgantown memorable.

My deepest gratitude to my fellow lab mates, Ashish, Ramanjaneyulu, Mayuri, Josh and Avinash, for their concern and delightful times in the lab. I am thankful to the post doctoral scholars in the lab Dr. Gugilla and Dr. Kababji for their guidance and valuable advice.

I love my friends, Adi, Perdi, Vamsi, Kedar, KC, Manu, Tanya, Anand, Abhi, Suji, Vasu, Lali and Tipu for always being by my side. Thanks to my numerous friends in Morgantown, who made me feel at home.

Last but definitely not the least I would thank my parents for their immense encouragement, moral support and belief. Also thank my loving Sister, Jiju and Brother for their care, love and for making sure they were just a phone call away.

Contents

CHAPTER 1	1
Introduction.....	1
1.1 Background.....	1
1.2 Purpose of Study	2
CHAPTER 2	3
Literature Review.....	3
2.1 Introduction	3
2.2 Fischer-Tropsch Synthesis	3
2.3 FTS Catalysts	5
2.4 FTS Catalyst Supports	5
2.5 Effect of Chemical Promoters on the Activity of Iron Catalysts	7
2.6 Catalyst Pretreatment	9
2.7 Fischer-Tropsch Reaction Kinetics.....	10
2.8 Operating Conditions and Product Selectivity.....	12
CHAPTER 3	15
Materials and Experimental-Statistical Procedures	15
3.1 Introduction.....	15
3.2 Preparation of Activated Carbon Support and its Pre-treatment	15
3.3 Preparation of Fe/AC Catalysts	16
3.4 Characterization of Catalyst.....	18
3.4.1 Surface Area and Pore Volume determination	18
3.4.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)	19
3.4.3 X-ray diffraction (XRD)	19
3.4.4 Energy-Dispersive X-ray Spectroscopy (EDS/EDX)	19
3.4.5 Temperature Programmed Reduction (TPR)	20
3.5 FTS activity.....	20
3.5.1 Experimental Setup.....	20
3.5.2 Experimental Procedure.....	22
3.5.3 Product Analysis	24
3.6 Data Analysis by Regression Analysis:	25

3.7 Safety Considerations	28
Chapter 4	29
Characterization Results	29
4.1 Introduction:.....	29
4.2 Surface Area and Pore Volume determination	29
4.3 SEM and EDX Characterizations	30
4.4 Temperature Programmed Reduction (TPR)	32
4.5 Summary	33
Chapter 5	34
FTS Activity Results	34
5.1 Introduction	34
5.2 Activity of Empty Reactor	35
5.3 Activity of AC support alone without any metal impregnation	35
5.4 Baseline catalyst (Fe-Mo-K-Cu/Anthracite AC).....	36
5.5 Effect of catalyst composition on FTS activity	39
5.5.1 Varying Fe Composition.....	39
5.5.2 Varying K composition	43
5.5.3 Varying Mo composition	48
5.5.4 Varying Cu composition	52
5.6 Summary	56
5.7 Data Analysis by Regression Analysis	57
5.8 Comparison of FTS activity using a Commercial AC (Norit ultra SX)	58
5.8.1. Effect on catalyst activity.....	59
5.8.2 Effect on yields of Hydrocarbons and Alcohols	61
Chapter 6	63
Conclusions and Future Work	63
6.1 Conclusions	63
6.2 Recommendations for Future Work.....	65
References:.....	66
Appendices.....	71
Appendix A: Trace Element Analysis of Support.....	72

Appendix B: Calculation Steps for Catalyst Preparation	74
Appendix C: Mass-Flow Controller Calibration Curves	76
Appendix D: Gas Chromatograph Operating Conditions	79
D.1.1 TCD calibration of gases	81
D.1.2 FID calibration of gases	82
Appendix E: Chromatograph Operating Conditions for Liquid Products.....	83
E.1.1 Organic Liquid (Oil) Phase Products	86
E.1.2 Aqueous Phase Products	86
Appendix F: Calculation Procedure for FTS Activity Results.....	87
F.1 Calculation procedure for Gas Analysis	88
F.1.2 FID gas analysis	88
Appendix G: Ft Activity Data for Catalysts with Varying Fe Composition	90
G.1 Gas phase and oil phase analysis results	91
G.2 Aqueous Phase Analysis	94
Appendix H: Ft Activity Data for Catalysts With Varying Potassium Composition.....	95
H.1 Gas phase and Oil phase Analysis results	96
H.2 Aqueous phase Analysis results	101
Appendix I: Ft Activity Data for Catalysts With Varying Molybdenum Composition	102
I.1 Gas phase and Oil phase Analysis results	103
I.2 Aqueous Phase analysis data:	108
Appendix J: Ft Activity Data for Catalysts With Varying Copper Composition.....	109
J.1 Gas and Oil phase analysis	110
J.2 Aqueous Phase analysis results:	113

List of Tables

Table 2.1: BET measurements results of activated carbon supports ²⁵	6
Table 2. 2 ^{6, 47} : Influence of Process Conditions and Catalyst Modifications on Selectivity in Fischer-Tropsch Synthesis	12
Table 3.1: Amount of Metal Salt Added per gram AC	17
Table 3.2: Catalyst Composition.....	18
Table 4.1 Results of BET measurements of Anthracite AC support and Baseline catalyst/AC...	30
Table 5.1: CO Conversion, CO ₂ Selectivity, H ₂ /CO Usage Ratio over baseline Fe-Mo-K-Cu/AC catalysts*	37
Table 5.2: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over baseline Fe-Mo-K-Cu/AC catalyst*.....	37
Table 5.3: Liquid Product Properties for the baseline Fe-Mo-K-Cu/AC catalyst*	39
Table 5.4: CO Conversion, CO ₂ Selectivity, H ₂ /CO Usage Ratio over different Fe-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*	40
Table 5.5: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over different Fe-Loaded Fe-Mo-K/Anthracite AC catalysts*	41
Table 5.6: Liquid Product Properties for Catalysts with Varying Fe Composition*	42
Table 5.7: CO ₂ Selectivity, H ₂ /CO Usage Ratio over different K-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*	44
Table 5.8: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over different K-Loaded Fe-Mo-K/AC catalysts*	45
Table 5.9: Liquid Product Properties for Catalysts with Varying K Composition*	47
Table 5.10: CO ₂ Selectivity, H ₂ /CO Usage Ratio over different Mo-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*	49
Table 5.11: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over different Mo-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*	50
Table 5.12: Liquid Product Properties for Catalysts of Varying Mo Composition*	51
Table 5.13: CO Conversion, CO ₂ Selectivity, H ₂ /CO Usage Ratio over different Cu-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*	53
Table 5.14: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over different Cu-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*	54

Table 5.15: Liquid Product Properties for Catalysts with Varying Cu Composition*	55
Table 5.16: Comparison of FTS activity of Catalysts supported on Anthracite based AC *	57
Table 5.17: R ² Values for the Regression Models	58
Table 5.18: Surface Area and Pore Volume of Activated Carbon Catalyst Supports	59
Table D. 1: Response Factor of TCD gas compounds.....	81
Table D. 2: Response Factor of FID gas compounds	82
Table E. 1: GC Operating Conditions for liquid product analysis.....	84
Table E.1. 1: Areas and Weights of Standard Alcohol Samples	86
Table G. 1: Selectivity and Production rate of Hydrocarbons for Varying Fe Composition.....	91
Table G. 2: Aqueous Phase results for Varying Fe Composition	94
Table H. 1: Selectivity and Production rate of Hydrocarbons for Varying K Composition.....	96
Table H. 2: Aqueous Phase results for Varying K Composition	101
Table I. 1: Selectivity and Production rate of Hydrocarbons for Varying Mo Composition.....	103
Table I. 2: Aqueous Phase results for Varying Mo Composition	108
Table J. 1: Selectivity and Production rate of Hydrocarbons for Varying Cu Composition	110
Table J. 2: Aqueous Phase results for Varying Cu Composition.....	113

List of Figures

Figure 2. 1 ³¹ : The variation of H ₂ /CO usage ratio with time on stream during FTS at 260°C, 1.5 MPa, GHSV= 1000 h ⁻¹	8
Figure 2. 2 ²⁵ : Effect of Mo loading on CO conversion at 300°C, 300psig, 3NI/gcat-h, H ₂ /CO=0.9	9
Figure 2.3 ³⁴ : Effect of pretreatment conditions on the hydrocarbon selectivity on a promoted iron catalyst (Fe/Cu/K/SiO ₂) @ 250°C, 1.45 MPa, H ₂ /CO ratio=0.67, 2 NI/gm-cat-hr.	10
Figure 2. 4 ⁶ : Hydrocarbon selectivity as function of the chain growth probability factor, α was calculated using Equation 2.13.	14
Figure 3.1: Schematic diagram of fluidized-bed reactor system	16
Figure 3.2: Experimental set-up to study the kinetics of Fischer-Tropsch Synthesis.....	21
Figure 3. 3: Schematic diagram of Catalyst bed	23
Figure 3. 4: F-Value	26
Figure 4.1: a) Scan at low magnification of the fresh baseline catalyst; (b) EDX comparison spectrum for rectangles marked in the image.	31
Figure 4.2: a) Scan at low magnification of the spent baseline catalyst; (b) EDX comparison spectrum for the fresh and spent baseline catalyst.....	31
Figure 4.3: TPR pattern of the AC-supported baseline catalyst	32
Figure 4.4: TPR pattern of the AC-supported catalysts with varying Fe Composition.....	33
Figure 5.1: CO conversion as a function of reaction time for the baseline Fe-Mo-K-Cu/AC catalyst (300°C, 300psig, syngas flowrate 100 sccm/min)	36
Figure 5.2: GC Plot of C ₁ – C ₅ Alcohols in aqueous phase using the baseline FeMoKCu/Anthracite AC catalyst.....	38
Figure 5.3: GC Plot of C ₅ – C ₂₆ hydrocarbons in organic phase using the baseline FeMoKCu/Anthracite AC catalyst.....	38
Figure 5.4: Effect of Fe loading on CO Conversion (300°C, 300psig, syngas flowrate 100 sccm/min).....	40
Figure 5.5: Effect of Fe loading on Hydrocarbon Selectivity (300°C, 300 psig, syngas flowrate 100 sccm/min; 24-48hrs)	41
Figure 5.6: Effect of Fe loading on alcohol distribution (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)	43

Figure 5.7: Effect of K loading on CO Conversion (300°C, 300psig, syngas flowrate 100 sccm/min).....	44
Figure 5.8: Effect of K loading on Hydrocarbon Selectivity (300°C, 300 psig, syngas flowrate 100 sccm/min; 24-48hrs)	46
Figure 5.9: Effect of K loading on alcohol distribution (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)	47
Figure 5.10: Effect of Mo loading on CO Conversion (300°C, 300psig, syngas flowrate 100sccm/min).....	48
Figure 5.11 : Effect of Mo loading on Hydrocarbon Selectivity (300°C, 300 psig, syngas flowrate 100 sccm/min; 24-48hrs)	50
Figure 5.12: Effect of Mo loading on alcohol distribution (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)	52
Figure 5.13: Effect of Cu loading on CO Conversion (300°C, 300psig, syngas flowrate 100sccm/min).....	53
Figure 5.14: Effect of Mo loading on Hydrocarbon Selectivity (300°C, 300 psig, syngas flowrate 100 sccm/min; 24-48hrs)	55
Figure 5.15: Effect of Cu loading on alcohol distribution (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)	56
Figure 5.16: Effect of Catalyst support on CO Conversion (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)	60
Figure 5.17: Effect of Catalyst support on yield of hydrocarbons and alcohols (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)	62
Figure C. 1: MFC calibration curve for He gas	77
Figure C. 2: MFC calibration curve for Hydrogen gas	77
Figure C. 3: MFC calibration curve for Syngas mixture (45%CO, 45%H ₂ , 5% Ar, 5%He).....	78

CHAPTER 1

Introduction

1.1 Background

Fischer-Tropsch (FT) synthesis is the process that converts synthesis gas, i.e. a mixture of carbon monoxide and hydrogen, into a wide range of long-chain hydrocarbons and oxygenates. As such FT synthesis constitutes a practical way for the chemical liquefaction of solid (coal) or gaseous (natural gas) carbon resources. Gas-to-liquid technology (GTL) via Fischer-Tropsch is currently one of the most promising topics in the energy industry due to the need to convert remote natural gas to environmentally clean liquid fuels. Interest in the Fischer-Tropsch technology is increasing since it is one of the key processes to meet future energy demand. SASOL in South Africa and Shell in Malaysia are among the large implementers of the FT process on a commercial scale.

The Fischer-Tropsch reaction is a heterogeneous catalytic reaction; under typical reaction conditions the reactants and products are present in gas and liquid phases and the catalyst itself is present as a solid. The FT reaction is a highly exothermic reaction, schematically represented as:

Also occurring is the water-gas shift (WGS) reaction:

In recent years, tailoring of FTS catalysts for the synthesis of diesel-range FT products has received attention. The catalytically active metals in Fischer-Tropsch synthesis are iron, cobalt, nickel and ruthenium. These are discussed in detail in coming chapters.

A variety of synthesis-gas compositions can be used. For cobalt-based catalysts the optimal H_2/CO ratio is around 1.8-2.1. Iron-based catalysts promote the water-gas shift (WGS) reaction. Therefore, iron-based catalysts can tolerate significantly lower ratios of H_2/CO .¹

The low-temperature FT process (LTFT) uses cobalt-based catalysts. It mainly produces vehicle-grade diesel and this process is applied in the SASOL GTL plants operating on low-grade coal in

South Africa. Industrial reaction conditions are 150-300°C and 25-40 bar. In contrast, the high-temperature FT process (HTFT), which operates at 300-345°C and relies on iron-based catalysts, mainly produces gasoline and chemicals. The Shell Middle Distillate operations in Malaysia are based on this process.²

1.2 Purpose of Study

Clean and very-low-sulfur fuels produced from domestic resources are of interest. Synthetic Fischer-Tropsch (FT) fuel is one type of fuel that can be produced from domestic resources such as natural gas, coal, petroleum coke, biomass and various wastes. The main purpose of this study is to produce such fuels from a domestic resource (coal), to be used in diesel engines or jet aircraft. In this research, the effectiveness and stability of Fe-based catalysts supported on activated carbon based on anthracite coal are studied for obtaining hydrocarbons from synthesis gas. The main focus is towards liquids in the range of C₉ through C₁₅ hydrocarbons, the kerosene/gasoline range sometimes called the single battlefield fuel. Oxygenates are also of interest.

The base case is a catalyst with a composition of 16wt% Fe, 6wt% Mo, 0.8wt% Cu and 0.9wt% K supported on activated carbon based on anthracite coal. The effect of the relative amounts of the supported metals (Fe, Mo, Cu, and K) and the properties of the support on the yield are investigated. The fresh catalyst is characterized by Brunauer Emmer Teller (BET) surface area, temperature-programmed reduction (TPR) and energy-dispersive x-ray spectroscopy (EDS or EDX).

The catalyst is tested in a computer-controlled fixed-bed reactor system. Typical reaction conditions are 300°C and 300psig with 6 NL/gcat/h syngas flowrate, after catalyst pretreatment at 400°C for 12h in hydrogen flow. The general FT reaction parameters, such as yield and selectivity of vapor and liquid hydrocarbons, conversion of syngas and usage ratio are investigated.

The specific aims of this project are:

- To study the effect of catalyst composition on activity
- To compare the results obtained using commercial activated carbon (Norit Ultra SX)

CHAPTER 2

Literature Review

2.1 Introduction

Increasing crude oil prices have caused a shift to coal and natural gas as the feed stock for the chemical industry. Coal and natural gas can be converted into syngas (a mixture of CO and H₂ gases) by partial oxidation or steam-reforming processes. The transformation of the syngas thus obtained into liquid fuels was first discovered by Franz Fischer and Hans Tropsch.³ The products of Fischer-Tropsch synthesis consist of a multi-component mixture of linear and branched hydrocarbons and oxygenated products; linear paraffins and α -olefins are the main products. Due to their very low aromaticity and zero sulphur content, the FT fuels are of high quality.⁴

The viability of any commercial process is generally governed by the performance of the catalyst used. In practice, the selection of a suitable catalyst is generally based on its costs, selectivity and stability. FT synthesis mainly uses cobalt-based and iron-based catalysts commercially. The major focus of most of the FT synthesis studies is on the optimization of metal function, with the aim of the maximal production of gasoline and diesel-range hydrocarbons.⁵

In this chapter, an introduction to FT synthesis and reactions involved in the process is presented. The selection of iron catalyst supported on activated carbon based on anthracite coal in this study, to produce the single battlefield fuel (SBF) which is used in jet aircraft, has been proposed by some of the previous studies from the literature. In addition, the kinetics of Fischer-Tropsch reactions and the product selectivity are discussed, based on previous studies from the literature.

2.2 Fischer-Tropsch Synthesis

The Fischer-Tropsch process is a chemical reaction in which syngas, a mixture of CO and H₂, is catalytically converted into a wide spectrum of hydrocarbon chains.

This type of product distribution has been explained assuming chain-growth polymerization, in which a step-by-step insertion of methyl, (-CH₂-) monomers occurs into the growing chain. The mechanism will be discussed in detail in further sections.

The main reactions leading to the formation of hydrocarbons during FTS can be written as follows:

the formation of paraffins :

the formation of olefins :

and the formation of alcohols and other oxygenates :

Water is a primary product of the FT reactions, and CO₂ can only be produced by the water-gas shift (WGS) reaction (Equation 1.2) which is a reversible parallel-consecutive reaction with respect to CO.⁶ WGS can be significant for K-promoted Fe-based catalysts and is negligible over Co-based and Ru-based catalysts.⁷

Other side reactions can be written as follows:

Methanation reaction,

Boudouard reaction,

Catalyst oxidation/reduction reaction,

Regarding the chemical equilibrium of the reactions involved, it can be stated as follows:

- Methane, the least desired product, is thermodynamically favoured over the other hydrocarbons,⁸
- The formation of alkanes is preferred over alkenes and alcohols,⁹

Therefore, the synthesis reaction has to be performed under kinetically controlled conditions in order to yield the desired hydrocarbons in significant amounts.

2.3 FTS Catalysts

As mentioned earlier, the most active metals for FT synthesis are Group VIII metals, namely cobalt, iron, ruthenium and nickel. Co and Ru are preferred for the synthesis of higher hydrocarbons at low temperatures and high pressure. However, despite the high catalytic activity of Ru, due to its high price and its limited world reserves compared to Co or Fe, Ru is not used commercially.¹⁰ Cobalt favors synthesis of straight-chain paraffins while iron produces paraffins, olefins and oxygenated products. Ni tends to form carbonyls at high pressures; with increasing temperatures, the selectivity changes to mainly methane.¹¹ The latter tendency is also observed with Co and Ru, but less so. With iron, the methane selectivity remains low even at high temperatures.¹²

Since cost considerations are a major driving force in selection of catalyst, iron usually has an obvious advantage over Co and Ni. Additionally, the syngas feed composition also governs the choice of catalyst. The high water-gas shift activity of iron-based catalysts makes it the preferred catalyst for converting hydrogen-lean syngas derived from coal (H_2 -to-CO molar ratios from 0.5 to 1.0). On the other hand, its high hydrogenation activity makes the cobalt-based catalyst the preferred one for converting hydrogen-rich syngas derived from natural gas (H_2 -to-CO molar ratios from 1.6 to 2.2).¹³ Among all the choices, however, iron-based catalysts are more versatile, owing to high catalyst activity and stability at low reaction temperature and less methane formation. However iron-based catalysts need alkali promotion for the production of olefins, oxygenates and branched hydrocarbons.¹⁴ Precipitated-iron catalysts and silica-supported cobalt catalysts have been proved as commercial catalysts.^{14, 15}

2.4 FTS Catalyst Supports

Catalyst supports are used to provide special attrition resistance at high temperature and pressure conditions.¹⁶ Many FT studies have reported using catalysts of iron supported on inorganic supports such as SiO_2 , Al_2O_3 , MgO and zeolites.^{17,18,19} Although these supports improve the structural stability of the iron catalysts, iron can react with the supports to form metal complexes, thus preventing complete reduction of all the iron and not allowing low loading of iron on the support.^{17,18,20} Hence it is also important to have a support which ensures complete reduction of

the metal. Other conditions, such as basicity, dispersion effect and electronic modification, also play a key role in choosing a catalyst support.

In this research, activated carbon (AC) was chosen as support due to its low metal-support interaction¹⁷ and its ability to restrict chain propagation, i.e., chain length could be limited below C₃₅.^{20,21} Further AC is easily available and it provides higher olefin/paraffin ratios.²² Vannice et al.²¹⁻²² initiated FT studies with iron catalysts supported on activated carbon. They reported that the use of carbon as support can not only prevent the reducibility problem but also provides very high dispersions of iron. This is important because Jung et al.²³⁻²⁴ report that very small unpromoted iron particles exhibit higher selectivity to olefins than bulk iron catalyst under comparable conditions.

Further, Ma et al.²⁵ report the effects of different sources of AC support. The four different supports used were derived from peat, generic wood, pecan shell and walnut shell. Some physical properties of the four ACs are listed in Table 2.1 below.²⁵

Table 2.1: BET measurements results of activated carbon supports²⁵

AC Source Type	Total SA (m ² /g)	Micropore SA (m ² /g)	f _{μS}	Total PV (cm ³ /g)	Micropore Vol. (cm ³ /g)	f _{μV}	Avg. pore dia. [Å]
Peat	606	45	0.75	0.48	0.22	0.46	59
Wood	970	914	0.94	0.58	0.44	0.76	66
Pecan	1016	736	0.72	0.72	0.36	0.50	51
Walnut	892	659	0.74	0.50	0.32	0.64	39

f_{μS}- fraction of surface area present in the micropores;

f_{μV}- fraction of pore volume present in the micropores

Catalysts supported on wood AC are the least active, with the smallest C₅₊ selectivity and the highest oxygenate selectivity, while catalysts supported on peat and pecan AC are the most active and produce the largest amount of hydrocarbons. The pecan-based support shows the best C₅₊ selectivity. Although the activity of the catalysts supported on walnut-shell AC is low, the C₅₊ selectivity is high.²⁵

2.5 Effect of Chemical Promoters on the Activity of Iron Catalysts

Metals such as Cu, Ru, Mo, and alkali oxides or carbonates of K and Rb are typically added to iron catalysts as promoters in order to improve catalytic properties. Structural promoters such as oxides (Al_2O_3 , SiO_2) are often added to stabilize a high metal surface area, to improve the mechanical properties and to prevent sintering of the catalyst during FT reactions.²⁶⁻²⁷ But catalysts containing structural promoters usually suffer from lower FT activity due to their strong metal-support-interactions.²⁷ Hence, to improve the performance of iron catalysts supported on activated carbon without sacrificing their activities and selectivities, chemical promoters such as K, Cu, and Mo are added. All these materials are used in this research work.^{5,7,28}

- **Potassium and Copper:** For iron-based catalysts, the basicity of the surface is of vital importance. The probability of chain growth increases with alkali promotion in the order Li, Na, K and Rb.⁸ Owing to the high price of Rb, potassium salts are used in practice.

The effect of potassium on the activity and product selectivity has been studied over a variety of iron catalysts. The general observations made include:^{10, 29, 30} (i) more heavy hydrocarbons, (ii) an increase in olefin selectivity, (iii) an increase in catalytic activity for water-gas shift (WGS) reactions, (iv) an increase in carbon deposition and catalyst deactivation rate, and (v) an increase in FT activity at low loadings of K, followed by decrease at higher loadings of K.

Iron catalysts are often promoted with copper, since it improves the rate of catalyst activation and shortens the induction period by reducing the reduction temperature for Fe.^{27, 30} Cu in fact does not act as a chemical promoter but instead provides a better dispersion of the active phase and a greater availability of active sites. When copper is present along with potassium, the FT and WGS activities are increased without significant change in selectivities.

Bukur et al.²⁷ found that K promoter enhances the olefin and heavy hydrocarbon selectivities due to the enhanced surface basicity, and Cu promoter facilitates the secondary reactions i.e., olefin hydrogenation and isomerization. Wan et al.³¹ reported that the addition of Cu promoter alone decreases the initial FTS activity and WGS activity, promotes the oxidation of iron carbide to magnetite, and hastens the deactivation of the iron catalyst, thus decreasing the FTS stability. But the addition of K promoter to Fe/Cu catalyst results in improved FTS and WGS activity and suppressed oxidation of iron carbides, thus resulting in improved FTS stability.

The H_2/CO usage ratio (ratio of moles of H_2 consumed to the moles of CO consumed) is a measure of WGS activity. The lower the ratio, the higher is the WGS activity. Figure 2.1³¹ shows the variation of H_2/CO usage ratio with time on stream for various catalysts. The usage ratio is lowest for the Fe/Cu/K catalyst. Therefore, the Fe/Cu/K has the highest WGS activity. Hence, using the Fe/Cu/K catalyst favors feeds having a lower H_2/CO ratio.

Figure 2. 1: The variation of H_2/CO usage ratio with time on stream during FTS at 260°C, 1.5 MPa, GHSV= 1000 h⁻¹ [31]

- Molybdenum:** Studies indicate that using Mo as promoter increases the activation of CO and tolerance towards sulfur poisoning for Fe-based catalysts and can produce high-quality liquid fuels in a one-step FT reaction.^{5, 32} Recently Ma et al.^{20, 25} found that Mo addition facilitates secondary reactions of olefins. They also reported the influence of Mo loading (0-12wt %) on the degree of reduction of iron, iron dispersion, activity, selectivity and stability. They concluded that the addition of Mo as promoter improves iron dispersion after catalysts are reduced at 400°C for 12h, thus preventing agglomeration of iron particles at reduction and reaction conditions. Larger amounts of Mo result in a decrease in surface area and an increase in pore diameter. Figure 2.2 suggests that the 6wt% Mo catalyst is more active than the 12wt% Mo catalyst.²⁵ Also, the WGS activity and selectivity towards olefins decreases with increase in Mo loading. More hydrocarbons and oxygenates are produced at lower loadings of Mo.

Figure 2. 2: Effect of Mo loading on CO conversion at 300°C, 300psig, 3NI/gcat-h, H₂/CO=0.9 ^[25]

2.6 Catalyst Pretreatment

Pretreatment is an important step in the development of an efficient catalyst. The catalyst performance in FT is affected by the phase of metal present in the catalyst.³³ After the synthesis step, most metals in the catalysts exist in the form of metal oxides which require an activation treatment to become active for FT synthesis. The common activation treatments for iron catalysts are H₂ reduction, CO reduction, or syngas-induced reduction. Fe and Co are predominantly reduced with H₂ at temperatures between 200°C and 500°C. Several studies have reported reduction of magnetite to metallic iron by H₂.³⁴⁻³⁵ Lox et al.³⁶ reported that H₂ reduction at 220°C results in 20% metallic iron. Bukur et al.^{13, 26, 27} studied various reducing gases and suggested that CO-reduced catalysts exhibit high initial activity and HC selectivity as compared to H₂-reduced catalysts, as shown in Figure 2.3 below.

Figure 2.3: Effect of pretreatment conditions on the hydrocarbon selectivity on a promoted iron catalyst (Fe/Cu/K/SiO₂) @ 250°C, 1.45 MPa, H₂/CO ratio=0.67, 2 NL/gm-cat-hr.³⁴

2.7 Fischer-Tropsch Reaction Kinetics

Various mechanisms have been proposed over the years. FT is a polymerization reaction which includes the following steps: ^{4, 10, 16, 37-40}

1. Reactant adsorption: In the first step, H₂ and CO species are assumed to adsorb on the catalyst surface and decomposes into hydrogen adatoms and adsorbed C and O respectively. The interaction between these surface species leads to the formation of several species like CH_x and OH as shown below (“s” denotes a surface species):

2. Chain initiation: The monomeric species CH_2 is formed from the adsorbed C and H on the catalyst surface. This step is the rate-determining step for CO hydrogenation kinetics. The CH_2 can be formed by one of the two 2-step reactions, as shown below:

3. Chain Growth or propagation: The CH_2 monomer species can either react with hydrogen to yield methane:

or link up with another CH_2 monomer to form an adsorbed C_2H_4 species:

This can further link up with another CH_2 unit forming adsorbed C_3H_6 unit and so on:

The probability that a molecule will continue reacting to form a longer chain is termed as the probability of chain growth (α) as used later.

4. Chain-growth termination or product desorption: The adsorbed species ($\text{C}_n\text{H}_{2n}\text{s}$) can desorb from the surface, forming olefins:

or can undergo hydrogenation forming paraffins ranging from methane to high-molecular-weight waxes:

Each of these options is a key step leading to chain termination.

Secondary reactions occur when a primary product desorbs from a site and interacts with another catalytic site before leaving the reactor. Schulz et al.^{11,40} showed the possible formation of paraffins as secondary products by the interaction of olefins with adsorbed species. The secondary reactions of olefins are given by⁴¹:

The mechanism in Equations 2.8 through 2.11 is based on the assumption that the basic building blocks or monomers of the FT reaction are the $-(CH_2)-$ units which are chemisorbed on the catalyst surface. Other mechanistic proposals presented by researchers are the surface carbide mechanism,^{42, 43} the enolic intermediate mechanism,⁴⁴ the CO-insertion mechanism,⁴⁵⁻⁴⁶ and the alkoxy intermediate mechanism.⁴¹

2.8 Operating Conditions and Product Selectivity

The FT reaction produces a wide range of hydrocarbons and oxygenated hydrocarbon products, irrespective of the operating conditions. The distribution of these products can be tuned to some extent by careful selection of the reaction temperature and pressure, the feed-gas composition, the space velocity, the type of catalyst and the amount or type of promoter present. Over the past two decades, extensive efforts have been made to improve the selectivity of FT catalysts for C_{5+} hydrocarbons to maximize gasoline-range or diesel-range hydrocarbons. The general influence of different parameters on the selectivity of hydrocarbons is listed in Table 2.2^{6, 47} below.

Table 2. 2: Influence of Process Conditions and Catalyst Modifications on Selectivity in Fischer-Tropsch Synthesis.^{6, 47}

Parameter	Chain length	Chain branching	Olefin Selectivity	Alcohol selectivity	Carbon deposition	Methane Selectivity
Temperature	↓	↑	*	↓	↑	↑
Pressure	↑	↓	*	↑	*	↓
H ₂ /CO ratio	↓	↑	↓	↓	↓	↑
Conversion	*	*	↓	↓	↑	↑
Space velocity	*	*	↑	↑	*	↓
Alkali content-iron catalyst	↑	↓	↑	↑	↑	↓
<i>Note: ↑, Increase with increasing parameter; ↓, Decrease with increasing parameter; *, Complex relation</i>						

In general,^{6, 47} a higher reaction temperature increases the rate of desorption, thus favoring the selectivity of lower-molecular-weight hydrocarbons, especially methane. Increasing the feed gas pressure results in increase to both the extent of conversion and the chain length of the products. At lower partial pressures of CO, the surface mobility of intermediate CH₂ monomer species is lower, hence the desorption probability of -(CH₂)_n- is higher. Higher partial pressure of H₂ increases the probability of chain termination by hydrogenation, thus forming more paraffins and decreasing the alkene selectivity.

The hydrocarbon yield is modeled by an Anderson-Schulz-Flory (ASF) distribution.¹⁰ The ASF distribution gives the chain length distribution, if the hydrocarbon is formed by the building-block mechanism by the addition of a (-CH₂-) intermediate monomer species with a constant growth probability, α ,⁴⁸ The ASF equation is as follows:

$$W_n = n \cdot (1 - \alpha)^2 \alpha^{n-1} \quad \dots 2.12(a)$$

In logarithmic form,

$$\log \left[\frac{W_n}{n} \right] = n \log \alpha + \text{constant} \quad \dots 2.12(b)$$

where W_n is the mass fraction of hydrocarbon with chain length n , and α is the growth probability factor, which is assumed independent of n and is defined by,⁴⁸

$$\alpha = \frac{R_p}{R_p + R_t} \quad \dots 2.13$$

where R_p and R_t are the rates of the propagation and termination reactions, given in Equation 2.10 and 2.11 respectively. The value of α determines the total carbon-number distribution of the FT product as shown in Figure 2.4.⁶ The value of α is dependent on the reaction conditions and the catalyst type. Dry et al.⁴⁹ reported typical ranges of α on Ru, Co and Fe of 0.85-0.95, 0.70-0.80, and 0.5-0.7 respectively. It was observed that α decreases with an increase in the reactor temperature.⁴⁹⁻⁵¹

Figure 2. 4: Hydrocarbon selectivity as function of the chain growth probability factor, α was calculated using Equation 2.13. ⁶

CHAPTER 3

Materials and Experimental-Statistical Procedures

3.1 Introduction

In this chapter, the procedure for synthesis of the catalyst support and the catalyst is described. In addition, different characterization techniques used for establishing the physical properties of the catalyst are mentioned. The various components of the experimental set-up are explained briefly with the technical specifications as provided by a manufacturer. Further, the experimental methodology is presented, followed by safety measures.

3.2 Preparation of Activated Carbon Support and its Pre-treatment

The activated-carbon support was prepared at the Fuel Cell laboratory at West Virginia University from anthracite coal with the help of Dr Zondlo, Dr Xu and Tristan McQuain. For completeness, a brief description of the equipment and procedure is given here. Carbon dioxide was used as the reactive gas in a fluidized-bed reactor which was designed and constructed in the laboratory. The schematic diagram of the fluidized-bed reactor system is shown in Figure 3.1

Figure 3.1: Schematic diagram of fluidized-bed reactor system

The quartz tube reactor was loaded with approximately 30 grams of powdered anthracite coal in the size range of (-40+70) mesh and placed in the furnace. Activation was performed in a two-stage process.⁵² In the first step, called carbonization, the temperature was ramped to 900°C at 400°C/hr in an inert nitrogen atmosphere. This was followed by activation at 900°C in a carbon dioxide atmosphere for 12 hours. Finally the reactor was cooled to room temperature under N₂ flow and disassembled. The sample was collected and weighed. A total of approximate 33g of this material was made available for the present work.

Following the activation step and before catalyst synthesis, the activated-carbon was thoroughly washed with deionized-water (DI) and dried overnight at 110°C, in order to remove any soluble impurities present on the support. The pretreated activated-carbon was stored in a sealed container and was used as the standard support for catalyst preparation in this study.

3.3 Preparation of Fe/AC Catalysts

All the catalysts investigated here were prepared using sequential incipient-wetness impregnation. In this method, an appropriate amount of metal salts (Table 3.1) was dissolved in

an amount of D.I. water equal to the pore volume of the support. This salt solution was added stepwise to the support. The order in which the metals were impregnated on the support is in the order of highest molecular weight of the metal salt to lowest molecular weight, i.e. Mo, Fe, Cu and K, as used by Ma et al.^{20, 25, 28} So for Mo impregnation, an appropriate amount of aqueous ammonium molybdate solution was impregnated on the activated carbon support. The material was then dried in air at 90°C overnight. Then aqueous solutions of ferric nitrate, cupric nitrate and potassium nitrate, corresponding to the final iron, copper and potassium contents on the catalyst were impregnated stepwise, followed by drying in air at the same temperature overnight.

Table 3.1: Amount of Metal Salt Added per gram AC

Promoter	Salt used	Composition (% Metal)	Amount of Salt (g/gAC)
Mo	Ammonium Molybdate (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	0	0
		6	0.111
		12	0.222
Fe	Ferric Nitrate Fe(NO ₃) ₃ ·9H ₂ O	0	0
		16	1.157
		32	2.314
Cu	Cupric Nitrate Cu(NO ₃) ₂ ·2.5H ₂ O	0	0
		0.8	0.0293
		1.6	0.058
K	Potassium Nitrate KNO ₃	0	0
		0.9	0.0233
		1.8	0.0466

Catalysts with compositions as listed in Table 3.2 were prepared and tested for FTS activity. These samples were chosen because of the limited amount of activated carbon support available and based on the results of prior work done in the lab using a commercial activated carbon. The baseline catalyst is highlighted in Table 3.2.

Table 3.2: Catalyst Composition

	Component wt%			
Sample ID	Fe	Mo	Cu	K
SG01	16	6	0.8	0.9
SG02	32	6	0.8	0.9
SG03	0	6	0.8	0.9
SG04	16	6	0.8	1.8
SG05	16	6	0.8	0
SG06	16	12	0.8	0.9
SG07	16	0	0.8	0.9
SG08	16	6	1.6	0.9
SG09	16	6	0	0.9

3.4 Characterization of Catalyst

After the synthesis step, the catalysts were characterized in order to obtain physical characteristics. Properties measured include pore structure/volume, surface area, elemental analysis and the active phase of the metal dispersion as described below.

3.4.1 Surface Area and Pore Volume determination

The pretreated activated carbon support and the fresh catalysts were tested with a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP) 2020 to determine the total surface area, the mesoporous area and the pore size distribution. A sample of about 0.1-0.2 grams is taken in a previously weighed sample tube and the total weight was recorded. The sample tube was evacuated to about 100 milliTorr and then backfilled with nitrogen twice using the

Micromeritics VacPrep 06. After the second backfill, it was degassed under vacuum at 300°C for one hour and cooled down to room temperature. The weight of the dried sample weight was recorded. The cooled sample tube was then connected to the ASAP 2020. The ASAP 2020 utilizes liquid nitrogen to do the adsorption tests. The analysis takes about 16 hours. The results are recorded at the completion of the analysis

3.4.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The pretreated activated carbon support was analyzed by Ken Stewart using a Varian CCD simultaneous ICP-OES (Vista Pro model) at NRCCE, WVU. Inductively coupled plasma optical emission spectrometry uses inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at characteristic wavelengths. The intensity of this emission is indicative of the concentration of the element within the bulk of the support. The technique can detect parts-per-million (ppm) quantities of inorganic elements on the catalyst support. The procedures of sample preparation and digestion are described in Standard Method 3030D.

3.4.3 X-ray diffraction (XRD)

XRD uses x-rays to find the crystalline structure, chemical composition, and physical properties of materials. X-ray diffraction measurements of the baseline catalyst before the reaction were carried out at room temperature (RT) by Gabriela Perhinschi using PANalytical X'Pert Pro X-ray Diffractometer with Cu K α radiation (1.54184Å). The instrument is equipped with a X'Celerator Detector System, Theta-Theta goniometer and 45 position sample changer. Software- controlled data acquisition systems (X'Pert High Score and X'Pert Quantify) were used for peak identification and profile searches. About 1-2 g of sample was taken on the sample holder and placed in the sample stager.

3.4.4 Energy-Dispersive X-ray Spectroscopy (EDS/EDX)

Energy-dispersive x-ray spectroscopy is an analytical technique used for elemental analysis. The surface morphology of the catalysts was determined by Adrienne MacLeod McGraw, using a

Hitachi S-4700 scanning electron microscope (SEM) at an accelerated voltage of 10kV. The SEM is equipped with an energy-dispersive spectrometer (EDS). The samples were prepared on a double-stick adhesive carbon tape mounted on specimen stubs and then sent into the SEM chamber. The samples are analyzed by EDS to confirm the presence and relative amounts of the elements.

3.4.5 Temperature Programmed Reduction (TPR)

Temperature-programmed reduction of catalyst was conducted by Dr Alaa Kababji in a Micromeritics AutoChem 2950 HP micro reactor at NETL, WV. The flowing stream contained 10% hydrogen (balance argon) at a flowrate of 50cm³/min. About 50 mg of catalyst is placed in a quartz U-tube. The sample is first pretreated under He by heating up to 275°C at 10°C/min for 4 h then cool to RT. The sample is then heated from RT to 1000°C at a constant rate of 10°C/min, no hold time. The corresponding H₂ consumption at each stage of reduction is quantified with peak areas using PEAKFIT software. A sharp peak in TPR is indicative of an instantaneous reduction process, whereas a broader peak is attributed to the longer time requirement for the reduction step.

3.5 FTS activity

3.5.1 Experimental Setup

The schematic diagram of the reactor system is shown in Figure 3.2. The reaction system is a computer-controlled setup located in a fume hood, and has been previously described in several journal articles.⁵³⁻⁵⁴ The computer uses the commercial software package InTouch by Wonderware. The unit has been designed to operate from atmospheric pressure to 1500 psig and temperatures up to 500°C. Almost all operating conditions are set from the computer directly. Reactor pressure is the exception and must be set manually. Data are logged by the computer at operator-determined intervals.

Figure 3.2: Experimental set-up to study the kinetics of Fischer-Tropsch Synthesis

The reactor is a stainless-steel tube (SS 304L) with 0.5”O.D. x 0.451”I.D. x 25”L specifications obtained from TW Metals, Inc.. The reactor is placed in an 18-inch single-zone furnace supplied by Applied Test Systems. The ends of the reactor are turned down to accept 1/2-inch Swagelok fittings.

Above the reactor, there is a piping sidearm which allows the reaction gases to flow in through the branch while holding a thermocouple vertically positioned in the straight run. An Inconel sheath ungrounded K-type thermocouple (model KQSS-116-18) with 1/16”D x 18”L specifications is used to read the catalyst bed temperature. A three-way valve (TV) is used to bypass the reactor. The unit has lines for feeding hydrogen, helium and syngas (45% H₂, 45% CO, 5% He and 5% Ar composition), each independently controlled by a Brooks 5850E mass-flow controller with an operating range of 0-200cc/min. Pressure gauges, obtained from Omega Engineering Inc., with operating range of 0-3000psig are used. The product stream from the reactor flows into a condenser. The condenser is operated with a cooling medium from a chiller maintained at 10°C. The liquids are collected while the gaseous products flow through a back-pressure regulator to the online gas chromatograph and the vent.

The entire unit is placed in a walk-in hood. The computer monitors alarms for CO and fire and the flows of reactive gases, hood velocity, ambient hood temperature, reactor pressure and electric power. The unit shuts down automatically in an event of hood failure, fire, power supply failure, or CO leak detection, or if gas flows or reactor temperature exceed preset operating ranges.

3.5.2 Experimental Procedure

Figure 3.3 shows a schematic diagram of the catalyst bed. Typically, about 1g of catalyst and 4g of 1/32-inch quartz chips (1:4wt dilution) are mixed together and placed in the center of the reactor with 1/16-inch quartz chips upstream and downstream of the catalyst-quartz mixture. The thermocouple is placed such that the tip touches the centre of the catalyst bed. The reactor is then mounted into the furnace.

Figure 3. 3: Schematic diagram of Catalyst bed

The system is then pressurized to 350 psig under He gas flow, and checked for leaks at room temperature. After the pressure leak test, the catalyst is pretreated by reducing in situ by H_2 at $400^\circ C$, 1 atm and 400sccm/min for 12h. Following the pretreatment, the reactor is cooled to $200^\circ C$ in flowing He, and then the system is pressurized to 300psig using the back pressure regulator. Once the reaction pressure is maintained, the He flow is cut off and syngas ($H_2/CO=1$) containing internal standards of 5% He and 5% Ar is introduced. The reaction flow rate is set in the computer. Finally, the reactor temperature is increased to the desired value and the run is started. The exit gas stream (unreacted syngas, CO_2 , hydrocarbons, water and alcohols) passes through a product trap/condenser maintained at $10^\circ C$ to condense liquid products. Non condensable gases pass through a back-pressure regulator and then either to a bubble flow meter or to a gas chromatograph (GC) for online product analysis. A liquid sample is collected every 24hr from the condenser and is analyzed in a separate gas chromatograph.

3.5.3 Product Analysis

Analysis of the inlet and outlet gases (He , H_2 , CO , CO_2 , CH_4 , and vapor-phase hydrocarbons) is accomplished on-line by a Clarus 500 gas chromatograph (GC) from Arnel, Inc. The sample is injected every 60 min. The GC uses a flame-ionization detector (FID) for the analysis of the vapor-phase hydrocarbons and a thermal-conductivity detector (TCD) for the analysis of the permanent gases (H_2 , CO_2 , N_2 , CO , He and Ar). Due to the large difference in thermal conductivity of helium (carrier gas) with reference to lighter hydrocarbons ($\text{C}_1\text{-C}_3$), these compounds are also detected by the TCD. The helium present in the feed is used as an internal standard for the analysis of H_2 and CO_2 . The argon is used as an internal standard for the analysis of CO and CH_4 . Also, the CH_4 signals as detected by the TCD and the FID are used to correlate the other gases obtained using only one detector. Thus the selectivities of all hydrocarbons formed can be obtained as shown in Appendix D.1.2. The operating conditions of the GC and the calibration procedures of the TCD and FID are mentioned in Appendix D.

The FT liquid sample collected is first separated off-line into an oil phase (the less-dense phase) and an aqueous phase (the denser phase). Then the weight of each phase is recorded prior to the product composition analysis.

The liquid products are analyzed off-line using a Varian 3400 GC. This GC is equipped with a MXT-2887 capillary column connected to a FID for the analysis of the organic phase (hydrocarbons) of the liquid sample, and a Tenax-TA packed column connected to FID for the analysis of the aqueous phase (water and oxygenates) of the liquid sample. A computer-based chromatography data system (Varian Star Chromatography Workstation) is used for data acquisition. The operating conditions of the GC are mentioned in Appendix E.

Prior to injection into the Varian GC, the oil phase samples are diluted with CS_2 to about 10wt% sample concentration. High purity CS_2 is used as a solvent here because of its miscibility with hydrocarbons, low boiling point and low response factor in the FID. The hydrocarbons are identified by matching retention times using the calibration curve as shown in Appendix E.1.1 and the detailed procedure of calculations is given in Appendix F.1.

For the analysis of the aqueous phase, the water present cannot be detected by the column used in the GC. Hence a known amount of internal standard is introduced to obtain a quantitative analysis of the sample. Cyclohexanol is used as the internal standard because it has long retention time and it is not produced by the FT reaction. Typically, 20 μl of cyclohexanol is

added to about 1ml of the aqueous sample taken in a GC vial. The weight of the sample and the weight of the cyclohexanol are recorded in order to determine the alcohol content in the FT sample. The process of calibration of GC for the aqueous product analysis is described in Appendix E.1.2. and the detailed procedure of the calculations is given in Appendix F.2.

3.6 Data Analysis by Regression Analysis:

The goal of regression analysis is to determine the values of parameters for a function that cause the function to best fit a set of data. A regression model is a statistical model which describes the variation in one or more variable(s) when one or more other variable(s) vary. In general a regression model is given by,

$$Y = f(X, \beta) \quad \text{.....(3.1)}$$

where Y is the dependent variable, X is the independent variable and the unknown parameters are denoted by β . In this work, stepwise regression by backward elimination is used. It is a process that deletes from the full model the predictor variables which add no significant predictive ability to the regression equation.

Some concepts used in stepwise regression of data are explained below:

Standard error of coefficients, S_{B_i} : It is a measure of accuracy of the regression model defined as:

$$S_{B_i} = \sqrt{\frac{\sum_n (y - y_p)^2}{(n - k - 1) \sum_n (x_i - \tilde{x}_i)^2}} \quad \text{.....(3.2)}$$

where, y is the observed value for the dependent variable

y_p is the predicted value of the dependent variable

x_i is the value of the independent variable of the i-th parameter

$\tilde{x}_i$ is the average value of the independent variable for the i-th parameter

n is the number of data points

k is the number of coefficients

Then (n-k-1) is the number of degrees of freedom

Coefficient of determination, R^2 : It provides a measure of how well future outcomes are likely to be predicted by the model. The value of R^2 ranges from 0 to 1. If the model is a poor fit, the value of R^2 will be close to 0; if the model fits the data well, the value of R^2 is close to 1. R^2 is defined as:

$$R^2 = \frac{\sum_n (y - \tilde{y})^2 - \sum_n (y - y_p)^2}{\sum_n (y - \tilde{y})^2} \quad \text{.....(3.3)}$$

where $\tilde{y}$ is the average value of the dependent variable.

F-value: It is used to test the significance of an independent variable. If the calculated F-value is bigger than the 4, maximum F-value entered as shown in figure 3.4 , then the predictor variable we test is significant and should be kept in the regression equation. F-value is defined by,

$$F = \left(\frac{B_i}{S_{B_i}} \right)^2 \quad \text{.....(3.4)}$$

Where, B_i is the coefficient of the i^{th} - variable in the regression equation.

Figure 3. 4: F-Value

A regression model was developed for the following dependent variables: CO conversion, olefin-to-paraffin ratio and yields of hydrocarbons and alcohols. Minitab 15 statistical software was used to do the stepwise regression. The following regression model was used:

$$Y = A_0 + A_1Fe + A_2Mo + A_3Cu + A_4K + A_5FeMo + A_6FeCu + A_7FeK + A_8MoCu + A_9MoK + A_{10}CuK + A_{11}FeMoCu + A_{12}FeMoK + A_{13}FeCuK + A_{14}MoCuK + A_{15}FeMoCuK + A_{16}Fe^2 + A_{17}Mo^2 + A_{18}Cu^2 + A_{19}K^2 \quad \dots(3.5)$$

The left-hand side contains the dependent/response variable (conversion, etc.). The right-hand side contains the independent/predictor variables (catalyst promoters) and the unknown coefficients.

In order to ease statistical bias, the values of Fe, Mo, Cu, K are normalized. The values of the parameters for the baseline catalyst were set to 1. The following equations are used to normalize the variables,

$$Fe_N = \frac{Fe}{16} \quad \dots(3.6a)$$

$$Mo_N = \frac{Mo}{6} \quad \dots(3.6b)$$

$$Cu_N = \frac{Cu}{0.8} \quad \dots(3.6c)$$

$$K_N = \frac{K}{0.9} \quad \dots(3.6d)$$

Thus the modified regression model:

$$Y = B_0 + B_1Fe_N + B_2Mo_N + B_3Cu_N + B_4K_N + B_5Fe_NMo_N + B_6Fe_NCu_N + B_7Fe_NK_N + B_8Mo_NCu_N + B_9Mo_NK_N + B_{10}Cu_NK_N + B_{11}Fe_NMo_NCu_N + B_{12}Fe_NMo_NK_N + B_{13}Fe_NCu_NK_N + B_{14}Mo_NCu_NK_N + B_{15}Fe_NMo_NCu_NK_N + B_{16}Fe_N^2 + B_{17}Mo_N^2 + B_{18}Cu_N^2 + B_{19}K_N^2 \quad \dots(3.7)$$

3.7 Safety Considerations

The following safety measures were followed while performing experiments,

1. Since the reactant gases used (H_2 and CO) are highly flammable, any source of ignition in the lab was avoided.
2. All gas lines and joints were checked periodically for any leaks, since the reactions are carried out at high pressure.
3. While performing experiments, the user wore personal protective equipment such as safety goggles, coat and safety gloves.
4. There are CO and hood alarms which are wired to the computer, so in the event of a gas release or hood failure the system shuts down by itself.
5. Handling of the compressed gas cylinders was performed appropriately. Cylinder caps were tightly fitted during cylinder replacements.
6. Material safety data sheets (MSDS) are available for all the possible chemicals to be used in the study including gases.
7. The regular maintenance of fume hood, eye-wash station, safety showers and fire extinguishers is carried out inside the lab area.
8. A list of personnel to be contacted in an emergency situation is posted near the entrance of the laboratory.

Chapter 4

Characterization Results

4.1 Introduction:

The interpretation of catalyst performance depends on the study of physical, chemical, and structural properties of the catalyst. The important catalytic properties of the synthesized catalysts are the catalyst composition, the BET surface area and the pore size distribution, metal dispersion, reducibility, crystal structure, surface morphology and oxidation state of the metals. In this chapter, the results of the characterization techniques mentioned in Section 3.4 are discussed.

4.2 Surface Area and Pore Volume determination

The BET specific surface area and pore volume of the AC support alone and the baseline catalyst before and after FT reaction are shown in Table 4.1. After the addition of Fe, Mo, Cu and K to the support, the BET surface area and the total pore volume of the fresh catalyst are reduced by 45% and 55% respectively. The decrease in BET surface area and pore volume for the fresh catalyst might be due to the filling of the metal precursors. For the spent catalysts, the BET surface area decreased by 85% and the pore volume decreased by 90%. This indicates that either the pores of the spent catalysts collapsed partially after FTS or the products remained in the micropores of the catalyst. These results are consistent with the findings of Ma et al.²⁰

Table 4.1 Results of BET measurements of Anthracite AC support and Baseline catalyst/AC

	BET Surface Area (m ² /g)	Large-Pore Surface Area (m ² /g)	Micropore Volume < 2.0 nm (cm ³ /g)	Macropore Volume > 2.0 nm (cm ³ /g)
Anthracite AC	1075	742	0.14	0.5
Fresh Baseline catalyst	591	408	0.063	0.225
After reaction Baseline catalyst	160	111	0.014	0.05

4.3 SEM and EDX Characterizations

As noted earlier, SEM gives information about the surface morphology of a sample, while EDAX will give information about the elemental composition of a sample. In the images the lighter areas are higher in metals (such as iron, molybdenum, copper and potassium) while the darker areas are richer in carbon.

Figure 4.1(a) is a scan at low magnification of the surface of the fresh baseline catalyst. The surface looks rough and rocky, and seems like small crystals. Further the areas marked within the white rectangles are magnified and scanned.

Figure 4.1(b) shows the EDX of these scans obtained at higher magnifications. The O peak is high for all the spots. The Fe, Mo, K, and Cu peaks seem to be almost about the same, the difference may be due to impregnation but most surfaces seemed to have uniform metal coating. The highest C peak was observed for the Pic 09 scan which is the relatively less coated surface. The Al and Si peaks come from their presence in the activated carbon itself.

Figure 4.1: a) Scan at low magnification of the fresh baseline catalyst; (b) EDX comparison spectrum for rectangles marked in the image.

Figure 4.2: a) Scan at low magnification of the spent baseline catalyst; (b) EDX comparison spectrum for the fresh and spent baseline catalyst

4.4 Temperature Programmed Reduction (TPR)

TPR patterns of iron-based catalysts supported on anthracite AC and commercial AC (Norit ultra SX) which were prepared by others in the lab are shown in Figure 4.3. The TPR patterns of all three catalysts shows a three-step reduction of iron oxide as shown below:²⁵

At 370°C-550°C the broad peak of the anthracite AC-supported catalyst suggests that all the oxide phases undergo a slow simultaneous reduction while the sharp peak of the commercial AC supported catalysts indicates that reduction is occurring stepwise and instantaneously.

Figure 4.3: TPR pattern of the AC-supported baseline catalyst

Figure 4.4: TPR pattern of the AC-supported catalysts with varying Fe Composition

4.5 Summary

The addition of metals to the support resulted in decrease in surface area and pore volume by 45% and 55% respectively. At the same time, the SEM evidence shows that the surface was coated uniformly throughout except for few relatively low metal coating spots. The TPR demonstrates that the all the oxides reduce simultaneously in a single step.

Chapter 5

FTS Activity Results

5.1 Introduction

The catalysts described in Table 3.2 were prepared and reacted in the system shown in Figure 3.2. For the purposes of this work, the most desired products are liquid hydrocarbons, followed by alcohols, while CO₂ and water are undesirable. Each run was carried out at the reaction temperature of 300°C, 300 psig pressure and a syngas (H₂/CO=1) flowrate of 6NI/gm-cat/h. The reactor effluent was sampled and analyzed by gas chromatography as described in Chapter 4

The results of all the runs are presented in terms of CO conversion, usage ratio, hydrocarbon selectivity, alcohol selectivity and hydrocarbon production rate. These are defined as follows.

$$\text{CO conversion (\%)} = \frac{\text{molar flow rate of CO consumption}}{\text{mole flow rate of CO inlet}} \times 100 \quad \dots(5.1a)$$

$$\text{H}_2 \text{ conversion (\%)} = \frac{\text{mole rate of H}_2 \text{ consumption}}{\text{mole rate of H}_2 \text{ inlet}} \times 100 \quad \dots(5.1b)$$

$$\text{Syngas conversion (mol\%)} = \frac{\text{mole rate of syngas consumption}}{\text{mole rate of syngas inlet}} \times 100 \quad \dots(5.1c)$$

$$\text{usage ratio of H}_2 \text{ to CO} = \frac{\text{mole rate of H}_2 \text{ consumption}}{\text{mole rate of CO consumption}} \quad \dots(5.2)$$

$$\text{Hydrocarbon productivity (g/kg cat - h)} = \frac{\text{hydrocarbon production rate}}{\text{catalyst mass (kg)}} \quad \dots(5.3)$$

$$\text{Selectivity of hydrocarbon with carbon number of n (wt\%)} = \frac{\text{rate of hydrocarbon with carbon number of n}}{\text{rate of hydrocarbon produced}} \times 100 \quad \dots(5.4)$$

$$\text{CO}_2 \text{ selectivity (mol\%)} = \frac{\text{mole rate of CO}_2 \text{ produced}}{\text{mole rate of CO consumption}} \times 100 \quad \dots(5.5)$$

Other selectivities are:

$$\text{alcohol selectivity (wt\%)} = \frac{\text{production rate of alcohols}}{(\text{production rate of alcohol} + \text{production rate of hydrocarbons})} \times 100 \quad \dots(5.6)$$

$$\text{rate of olefin to paraffin} = \frac{\text{production rate of olefin}}{\text{production rate of paraffin}} \quad \dots(5.7)$$

In this chapter the topics discussed are the results using the empty reactor, activated carbon alone, and all the catalysts. The FTS performances of the catalysts with varying compositions are compared. These catalysts, with the anthracite-based activated-carbon support are also compared to results from the WVU laboratory with catalysts using a commercial activated-carbon (Norit ultra SX). Since during the first 24 hours, products with high selectivity of the lower hydrocarbons are produced and the catalyst seems to be deactivating after 48 hours eventually. Thus, the data reported in the following sections correspond to time on stream between 24 and 48h because products with high selectivity to higher hydrocarbons were produced. Further, for ease in discussion, individual products are lumped into groups which are discussed below.

5.2 Activity of Empty Reactor

First, the empty reactor was run using the standard reaction gases and conditions. The reactor was found to have minimal catalytic activity. Conversion of CO did not exceed 0.8% in any instance. Moreover, no peaks were detected on the FID, and no detectable liquid was collected.

5.3 Activity of AC support alone without any metal impregnation

The FT reaction was carried out on the activated carbon support alone (with no metals impregnated). Again the standard reaction gases and conditions were used to determine any

activity due to the various components in the AC support. The AC support was also found to have minimal catalytic activity. The CO conversion did not exceed 0.9% at any instance. Also, no peaks were detected on the FID and no detectable liquid was collected.

5.4 Baseline catalyst (Fe-Mo-K-Cu/Anthracite AC)

The FT reaction was carried out on the baseline Fe/AC catalyst, SG01 as listed in Table 3.2., under the same conditions. The catalyst showed moderate catalytic activity, (see Figure 5.1), and made CO₂, moderate amounts of water, large amounts of hydrocarbons, and small amount of alcohols.

Figure 5.1: CO conversion as a function of reaction time for the baseline Fe-Mo-K-Cu/AC catalyst (300°C, 300psig, syngas flowrate 100 sccm/min)

Individual weights of the components of the outlet stream are given in Appendix G. The performance of the baseline catalyst is summarized in Tables 5.1-5.3.

Ma et al.²⁸ showed that the overall CO consumption rate, r_{CO} and CO₂ formation rate, r_{CO_2} could be related to the FTS reaction rate, r_{FTS} , and the WGS rate, r_{WGS} , by:

$$-r_{\text{CO}} = N_{\text{CO,in}} - N_{\text{CO,out}} = r_{\text{FTS}} + r_{\text{WGS}} \quad \dots\dots\dots(5.8)$$

and, $r_{\text{WGS}} = r_{\text{CO}_2} \quad \dots\dots\dots(5.9)$

Hence, average CO₂ selectivity in Table 5.1 mirrors the extent of WGS activity in the FTS system. In this case, owing to the high CO₂ selectivity of the baseline catalysts, water-gas shift activity is expected to be high.

Table 5.1: CO Conversion, CO₂ Selectivity, H₂/CO Usage Ratio over baseline Fe-Mo-K-Cu/AC catalysts*

CO Conversion, mol%	CO ₂ Selectivity, mol%	(H ₂ /CO) usage ratio
45	56.4	0.81

*Average taken from the 24-48 hour balance

Table 5.2: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over baseline Fe-Mo-K-Cu/AC catalyst*

Hydrocarbon Selectivity (wt%)			Hydrocarbon Productivity, g-HC/kg-cat/h	Olefin/Paraffin Ratio	
CH ₄	C ₂ -C ₄	C ₅ +		C ₂ -C ₄	C ₆ -C ₁₄ (liq)
18.8	56.5	24.7	346	1.8	0.6

*Average taken from the 24-48 hour balance

The liquid product contains hydrocarbons from C₅-C₂₆ in the organic phase and C₁-C₅ alcohols in the aqueous phase. The chromatograms from these liquids are shown in Figures 5.2 and 5.3.

Figure 5.2: GC Plot of C₁ – C₅ Alcohols in aqueous phase using the baseline FeMoKC_u/Anthracite AC catalyst.

Figure 5.3: GC Plot of C₅ – C₂₆ hydrocarbons in organic phase using the baseline FeMoKC_u/Anthracite AC catalyst

The quantitative analysis of the products is summarized in Tables 5.2 and 5.3. From these data, the hydrocarbon production rate is about two orders of magnitude greater than the alcohol production rate. The mass balance closures over the baseline catalysts were about $100\pm 0.8\%$.

Table 5.3: Liquid Product Properties for the baseline Fe-Mo-K-Cu/AC catalyst*

Total Alcohol Weight (mg)	Alcohol in FT sample (wt %)	Total Oil Weight (mg)	Alcohol Selectivity (%)	Alcohol Production rate (g/kg-cat-hr)
400	43.2%	1000	2.08	7.2

*Average taken from the 24-48 hour balance

5.5 Effect of catalyst composition on FTS activity

5.5.1 Varying Fe Composition

The CO conversions of the catalysts with changing Fe content (SG01-SG03 as listed in Table 3.2) are shown in Figure 5.4 as a function of reaction time. The activity is observed to increase with increase in Fe content, but the increase is small for Fe loadings greater than 16 wt%.

Figure 5.4: Effect of Fe loading on CO Conversion (300°C, 300psig, syngas flowrate 100 sccm/min)

The total product distribution for this series of catalysts is given in Appendix G. Table 5.4 summarizes the gas phase analysis. CO₂ selectivity, and hence water-gas shift activity, increase when the Fe composition is increased.²⁸ Further the effects of Fe addition on the catalyst productivity and selectivities are shown in Table 5.5.

Table 5.4: CO Conversion, CO₂ Selectivity, H₂/CO Usage Ratio over different Fe-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*

%Fe	0	16	32
CO Conversion,%	3	45	51
CO ₂ Selectivity, mol%	Not detected	56.4	66
(H ₂ /CO) usage ratio	1.3	0.81	0.79

*Average taken from the 24-48 hour balance

Table 5.5: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over different Fe-Loaded Fe-Mo-K/Anthracite AC catalysts*

%Fe	0	16	32
Productivity, g-HC/kg-cat/h	0	346	396
Hydrocarbon Selectivity (wt%)			
CH ₄	0	18.8	18.9
C ₂ -C ₄	0	56.5	51.5
C ₅ +	0	24.1	29.7
C ₆ -C ₈ (liq)	0	4.1	8.4
C ₉ -C ₁₅ (liq)	0	7.0	8.9
Olefin/Paraffin Ratio			
C ₂ -C ₄	0	1.8351	1.6
C ₆ -C ₁₄ (liq)	0	0.577	0.35

Figure 5.5: Effect of Fe loading on Hydrocarbon Selectivity (300°C, 300 psig, syngas flowrate 100 sccm/min; 24-48hrs)

Corresponding to the highest activity (as shown in Figure 5.4), the 32% Fe catalyst exhibits the highest hydrocarbon productivity. However, that catalyst shows higher methane selectivity, low C₂-C₄ selectivity but higher C₅₊ selectivity (Figure 5.5). Further the increase in Fe composition results in a decrease in C₂-C₁₄ olefin selectivity.

Table 5.6 summarizes the quantitative analysis of the liquid products. The effect of Fe loading on the yields of hydrocarbon and alcohol is shown in Tables 5.5 and 5.6. As expected, the 32% Fe exhibits the highest productivities of hydrocarbon (396 g/kg-cat/h) and alcohol (18.8 g/kg-cat/h). This is consistent with the high activity of the catalyst. While, the values of alcohol selectivity as shown in Table 5.6 for all three catalysts are less than 4%, it increases with Fe loading. These results indicate the hydrocarbons make up the bulk of the products.

Table 5.6: Liquid Product Properties for Catalysts with Varying Fe Composition*

% Fe	Total Oil Weight (mg/day)	Total aqueous Weight (mg/day)	Alcohol in FT sample (wt %)	Alcohol Selectivity (%)	Alcohol Production rate (g/kg-cat-hr)
0%Fe	0	0	-	-	-
16%Fe	1000	400	43.00%	2.03	7.2
32%Fe	1720	2582	17.50%	4.54	18.8

*Average taken from 24-48 hr balance

No liquid products were collected for 0% Fe. For the two remaining catalysts the distribution of individual C₁-C₅ straight alcohols is shown in Figure 5.6. C₃-C₅ branched alcohols were also detected and quantified, but the amounts are small and are not shown here. As can be seen from Figure 5.6, ethanol is the dominant alcohol for both catalysts, followed by C₁-OH, C₄-OH, C₃-OH and C₅-OH. This quantitative sequence of alcohol selectivity was also reported by Ma et al.²⁸ The distribution of alcohols decreases with the increase in Fe loading but the overall alcohol selectivity with respect to hydrocarbons increases.

Figure 5.6: Effect of Fe loading on alcohol distribution (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)

5.5.2 Varying K composition

The effects of K loading on the activity of catalysts SG01, SG04 and SG05 (as listed in Table 3.2) are shown in Figure 5.7. For the 0.9%K catalyst, the CO conversion is higher than the 0%K catalyst but the former deactivates faster. On the other-hand, on increasing the K loading further (1.8%K), the conversion decreases and also results in rapid deactivation. This result is consistent with the finding by Ma et al.²⁸ that a small amount of potassium increases FTS activity, while a larger amount decreases FTS activity. The amounts of individual components of the product stream are given in Appendix H.

Figure 5.7: Effect of K loading on CO Conversion (300°C, 300psig, syngas flowrate 100 sccm/min)

The average values of CO₂ selectivity and the usage ratio are listed in Table 5.7. It can be observed that 0%K showed maximum CO₂ selectivity with least usage ratio, thus resulting in the highest water-gas shift activity.

Table 5.7: CO₂ Selectivity, H₂/CO Usage Ratio over different K-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*

%K	0	0.9	1.8
CO Conversion, mol%	36.5	44.5	30
CO ₂ Selectivity, mol%	58.46	56.4	56.5
(H ₂ /CO) usage ratio	0.78	0.81	0.83

*Average taken from the 24-48 hour balance

The effects of K loading on the catalyst productivity and selectivities between 24h and 48h are shown in Tables 5.8 and 5.9. From Table 5.8 the hydrocarbon production rate is about the same with addition of a small amount of K but decreases with addition of more K. The selectivity of C₁-C₄ hydrocarbons is observed to decrease with addition of K. Correspondingly, the selectivity of C₅₊ hydrocarbons increases with the addition of K (as shown in figure 5.8) These results are consistent with previous studies of potassium on iron-based catalysts.^{5, 27-28, 41}

Table 5.8: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over different K-Loaded Fe-Mo-K/AC catalysts*

%K	0	0.9	1.8
Productivity, g-HC/kg-cat/h	336	346	200
	Hydrocarbon Selectivity (wt %)		
CH ₄	30.2	18.8	13.8
C ₂ -C ₄	57.5	56.5	52.5
C ₅₊	12.2	24.1	33.7
C ₆ -C ₈ (liq)	1.0	4.1	13.0
C ₉ -C ₁₅ (liq)	1.3	7.0	1.6
	Olefin/Paraffin Ratio		
C ₂ -C ₄	1.05	1.8351	0.9564
C ₆ -C ₁₄ (liq)	0.384	0.577	0.318

*Average taken from the 24-48 hour balance

Figure 5.8: Effect of K loading on Hydrocarbon Selectivity (300°C, 300 psig, syngas flowrate 100 sccm/min; 24-48hrs)

Several FT studies of potassium-promoted iron catalysts report that addition of potassium enhances CO adsorption and restricts H₂ adsorption, thus resulting in formation of heavier hydrocarbons.^{27-28, 37, 44} The small CO conversion and high carbide formation for the 1.8%K catalyst results in a lower methane selectivity but more C₅₊ hydrocarbons.

The ratios of olefins to paraffins for the three catalysts are also presented in Table 5.8. These values show a large increase for the 0.9%K catalyst relative to the 0%K catalyst, but only a small increase when the 1.8%K is used relative to the 0.9%K catalysts. Therefore, it can be concluded that a small amount of potassium increases the formation of primary olefins, while a larger amount of potassium results has a smaller effect. This observation is consistent with several studies of the potassium effect.^{5, 27-28, 37, 44}

From Table 5.9 the unpromoted catalyst results in about the same alcohol selectivity relative to 0.9%K. But on doubling the K loading, alcohol selectivity increases by a factor of 3. These results were found to be consistent with the findings of Ma et al.²⁸

Table 5.9: Liquid Product Properties for Catalysts with Varying K Composition*

%K	Total Alcohol Weight (mg)	Alcohol in FT sample, wt%	Total Oil Weight (mg)	Alcohol Selectivity (%)	Alcohol Production rate, (g/kg-cat/hr)
0%	1165	15.81%	202	2.24	7.67
0.9%	400	43.08%	1000	2.08	7.18
1.8%	1500	24.00%	1000	6.69	15.0

*Average taken from the 24-48 hour balance

The distribution of individual C₁-C₅ straight alcohols is shown in Figure 5.9. C₃-C₅ branched alcohols were also detected and quantified, but the amounts are small and are not shown here. As can be seen from Figure 5.9, ethanol is the dominant alcohol for all three catalysts, followed by C₁-OH, C₃-OH, C₄-OH and C₅-OH. This qualitative sequence of alcohol selectivity was also

Figure 5.9: Effect of K loading on alcohol distribution (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)

5.5.3 Varying Mo composition

The effects of Mo loading on activity of the catalysts SG01, SG06 and SG07 (as listed in Table 3.2) are shown in Figure 5.10. The unpromoted catalyst results in low CO conversion and deactivates soon. The 6%Mo catalyst starts at 70% CO conversion but decreases with time, having an average conversion of 45% in 72 h. The 12%Mo catalyst starts at 20%, and drops to half that in 72 h.

Figure 5.10: Effect of Mo loading on CO Conversion (300°C, 300psig, syngas flowrate 100sccm/min)

Table 5.10 lists the average values of CO conversion, CO₂ selectivity and H₂/CO usage ratio. The 12%Mo catalysts shows the highest CO₂ selectivity and least H₂/CO usage ratio. This suggests that the extent of WGS is increased to some extent on the 12%Mo catalyst. The increase of the (H₂/CO) usage ratio with increase in Mo loading is consistent with the finding of Ma et al.²⁵ using AC supported Fe-Mo-Cu-K catalysts.

Table 5.10: CO₂ Selectivity, H₂/CO Usage Ratio over different Mo-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*

%Mo	0	6	12
CO Conversion, %	0.3	44.5	10.5
CO ₂ Selectivity, mol%	0	56.4	66
(H ₂ /CO) usage ratio	1.25	0.81	0.72

*Average taken from the 24-48 hour balance

The effects of Mo loading on the catalyst productivity and selectivities are shown in Tables 5.11 and 5.12. The data collected corresponds to time on stream between 24h and 48h. The amounts of individual components in the outlet stream are given in Appendix I. Corresponding to the highest activity (as shown in Figure 5.8), the 6% Mo catalyst exhibits the highest hydrocarbon productivity. The selectivity of C₂-C₄ hydrocarbons is observed to increase with the addition of a small amount of Mo, and decreases with addition of more Mo. The 12% Mo catalyst shows higher methane selectivity as well as higher C₅₊ hydrocarbon selectivity (as shown in Figure 5.11). The increase in methane selectivity for the 12% Mo catalyst is not consistent with the previous studies of molybdenum on iron-based FT catalysts.^{20, 25} But the increase in selectivity of C₅₊ hydrocarbons with increase in Mo loading remains consistent with the findings of Ma et al.^{20, 25} According to Ma et al. the increased selectivity of higher molecular-weight hydrocarbons over the 12% Mo catalyst is due to the lower catalyst activity.

The olefin-paraffin ratio is observed to decrease with increase in Mo loading. Ma et al.^{20, 25} reported that Mo promotion facilitates the secondary reactions of olefins, resulting in a decrease in the selectivity of olefins with an increase in Mo loading. Therefore, these results remain consistent with the findings of Ma et al.^{20, 25}

Table 5.11: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over different Mo-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*

%Mo	0	6	12
Productivity g-HC/kg-cat/h	0	346	65
Hydrocarbon Selectivity (wt %)			
CH ₄	0	18.8	22.4
C ₂ -C ₄	0	56.5	47.9
C ₅ +	0	24.1	29.7
C ₆ -C ₈ (liq)	0	4.1	6.4
C ₉ -C ₁₅ (liq)	0	7.0	8.8
Olefin/Paraffin Ratio			
C ₂ -C ₄	0	1.8351	1.84
C ₆ -C ₁₄ (liq)	0	0.577	0.38

Figure 5.11 : Effect of Mo loading on Hydrocarbon Selectivity (300°C, 300 psig, syngas flowrate 100 sccm/min; 24-48hrs)

The quantitative analysis of the liquid products is summarized in Table 5.12. Owing to the high activity of the 6% Mo catalyst (see Figure 5.10), it exhibits the highest productivities of hydrocarbon (346 g/kg-cat/h) and alcohol (7.2 g/kg-cat/h). For all three catalysts, the alcohol selectivity is less than 5 wt%, but the selectivity increases with Mo loading. Hence, these results indicate that hydrocarbons and water make up the bulk of the products, but the Mo promoter improves oxygenate selectivity. This result is consistent with the finding by Ma et al.^{20, 25}

Table 5.12: Liquid Product Properties for Catalysts of Varying Mo Composition*

%Mo	Total Alcohol Weight (mg)	Alcohol in FT sample, wt%	Total Oil Weight (mg)	Alcohol Selectivity, (wt%)	Alcohol Production rate, g/kg-cat/h
0%	0	-	0	-	-
6%	400	43.08%	1000	2.08	7.2
12%	600	13.18%	260	4.9	3.3

*Average taken from the 24-48 hour balance

No liquid products were produced using the 0%Mo catalyst. For the remaining two catalysts, the distribution of individual C₁-C₅ straight alcohols is shown in Figure 5.12. C₃-C₅ branched alcohols were also detected and quantified, but the amounts are small and are not shown here. As can be seen from Figure 5.12, ethanol is the dominant alcohol for all three catalysts followed by C₁-OH, C₃-OH, C₄-OH and C₅-OH. This quantitative sequence of alcohol selectivity was also reported by Ma et al.^{20, 25}

Figure 5.12: Effect of Mo loading on alcohol distribution (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)

5.5.4 Varying Cu Composition

The effects of Cu loading on activity of the catalysts SG01, SG08 and SG09 (as listed in Table 3.2) are shown in Figure 5.13 and summarized in Table 5.13. All the three catalysts show similar activity. The unpromoted catalyst results in lower CO conversion, as compared to the promoted catalysts. On addition of small amounts of copper, the increase in activity is rather small, less than about 5%. The CO₂ selectivity increases slightly with the addition of copper. These results were found to be consistent with the several works done on promotional effects of Cu on iron-based catalysts.^{27, 31}

Figure 5.13: Effect of Cu loading on CO Conversion (300°C, 300psig, syngas flowrate 100sccm/min)

Table 5.13: CO Conversion, CO₂ Selectivity, H₂/CO Usage Ratio over different Cu-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*

%Cu	0	0.8	1.6
CO Conversion, mol%	40.3	44.5	43.2
CO ₂ Selectivity, mol%	55.8	56.4	58.4
(H ₂ /CO) usage ratio	0.86	0.81	0.81

*Average taken from the 24-48 hour balance

The effect of Cu loading on the catalyst productivity and selectivities are shown in Tables 5.14 and 5.15. The data reported correspond to the time on stream between 24 and 48 h. The amounts of the individual components in the product stream are given in Appendix J. Corresponding to the highest activity (as shown in Figure 5.13), the baseline 0.8% Cu catalyst exhibits the highest hydrocarbon production rate as shown in Table 5.14. Selectivity of C₁-C₄ hydrocarbons increases slightly with Cu loading. C₅₊ hydrocarbons selectivity decreases slightly with Cu loading (as shown in Figure 5.14)

Table 5.14: Productivity and Selectivity of Hydrocarbon and Olefin-to-Paraffin ratio over different Cu-Loaded Fe-Mo-K-Cu/Anthracite AC catalysts*

%Cu	0	0.8	1.6
Productivity g-HC/kg-cat/h	278	346	295
	Hydrocarbon Selectivity (wt %)		
CH ₄	16	18.8	20
C ₂ -C ₄	53	56.5	59.6
C ₅₊	32.0	24.1	19.9
C ₆ -C ₈ (liq)	7.1	4.1	2.6
C ₉ -C ₁₅ (liq)	8.4	7.0	3.6
	Olefin/Paraffin Ratio		
C ₂ -C ₄	1.62	1.7	1.60
C ₆ -C ₁₄ (liq)	0.4	0.58	0.38

*Average taken from the 24-48 hour balance

Figure 5.14: Effect of Mo loading on Hydrocarbon Selectivity (300°C, 300 psig, syngas flowrate 100 sccm/min; 24-48hrs)

From Table 5.15, the 0.8% Cu catalyst results in the lowest alcohol selectivity. Also, for all three catalysts the alcohol selectivity is less than 5 wt%.

Table 5.15: Liquid Product Properties for Catalysts with Varying Cu Composition*

% Cu loading	Total Alcohol Weight (mg)	Alcohol in FT sample (wt%)	Total Oil Weight (mg)	Alcohol Selectivity (wt %)	Alcohol Production rate (g/kg-cat-h)
0%	1242	21.87%	1090	3.92	11.32
0.8%	400	43.08%	1000	2.08	7.18
1.6%	1100	19.90%	480	3	9.12

*Average taken from the 24-48 hour balance

Figure 5.15 shows the distribution of individual C₁-C₅ straight alcohols for all three catalysts. C₃-C₅ branched alcohols were also detected and quantified, but the amounts are small and are not shown here. As can be seen from the Figure 5.15, ethanol is the dominant alcohol for all three catalysts followed by C₁-OH, C₃-OH, C₄-OH and C₅-OH. This quantitative sequence of alcohol selectivity was also reported by Ma et al.^{20, 25}

Figure 5.15: Effect of Cu loading on alcohol distribution (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)

5.6 Summary

The FTS activity for catalysts with varying compositions supported on AC based on anthracite coal was studied at reaction temperature 300°C, reactor pressure 300psig and syngas flowrate 100 sccm/min. Table 5.16 summarizes the activity of all the catalysts. On increasing the Fe loading, the FT activity and the yields of hydrocarbons and alcohols increase. The Mo promotion

results in a decrease in the activity. Varying the copper loading does not result in much difference in the activity. The FT activity decreases on doubling the potassium loading and does not result in much difference when potassium is removed.

Table 5.16: Comparison of FTS activity of Various Catalysts supported on Anthracite based AC *

Catalyst	Average CO Conversion, mol%	Alcohol Production rate, g/kg-cat/h	Hydrocarbon Production rate, g/kg-cat/h
Baseline: 6%Mo 16%Fe 0.8%Cu 0.9%K	45.00	7.8	346
6%Mo 0%Fe 0.8%Cu 0.9%K	3.00	0	0
6%Mo 32%Fe 0.8%Cu 0.9%K	51.00	18.2	396
0%Mo 16%Fe 0.8%Cu 0.9%K	0.30	0	0
12%Mo 16%Fe 0.8%Cu 0.9%K	10.50	3.3	65
6%Mo 16%Fe 0%Cu 0.9%K	40.30	11.3	278
6%Mo 16%Fe 1.6%Cu 0.9%K	43.20	9.1	295
6%Mo 16%Fe 0.8%Cu 0%K	36.50	7.7	336
6%Mo 16%Fe 0.8%Cu 1.8%K	30.00	15	200

*Average taken from 24-48h balance

5.7 Data Analysis by Regression Analysis

The parameters and procedure involved are described in Section 3.6. Briefly, the intent is to find simple expressions for CO conversion, olefin-to-paraffin ratio, and yield of hydrocarbons and alcohols that are statistically meaningful.

For the CO conversion, the equation was determined to be:

$$\text{Conversion (mol\%)} : 4.867 + 24\text{Fe}_N \quad (5.10)$$

For the yield of hydrocarbons, the equation was determined to be:

$$\text{Hydrocarbon Production rate (gHC/kg - cat/h)} : 14.89 + 198\text{Fe}_N \quad (5.11)$$

For the yield of alcohols, the equation was determined to be:

$$\text{Alcohol Production rate (gHC/kg - cat/h)} : -1.056 + 9.1\text{Fe}_N \quad (5.12)$$

Equations 5.10-5.12 indicate that amount of iron plays a vital role. CO Conversion and yield of hydrocarbons and alcohols increases with the increase in iron loading.

For the olefin-to-paraffin ratio, the equation was determined to be:

$$\text{O/P ratio} : 0.3068 + 0.86\text{Fe}_N\text{Mo}_N \quad (5.13)$$

This indicates that the most important term for the O/P ratio is the interaction between Fe and Mo. Table 5.17 contains the R^2 values for the expressions (5.10-5.13). The R^2 values are very low but this analysis gives a quantitative idea about the parameters to be optimized.

Table 5.17: R^2 Values for the Regression Models

Property	R^2 Value
Conversion	0.38
Hydrocarbon Production rate	0.41
Alcohol production rate	0.52
O/P ratio	0.69

5.8 Comparison of FTS activity using a Commercial AC (Norit ultra SX)

In this section, the activity of catalysts using the in-house AC support derived from anthracite coal, presented in this work is compared with similar work done in the laboratory using a commercial AC support (Norit Ultra SX).

Table 5.18 compares the morphology of the two AC catalyst supports. The BET areas of the two supports are approximately equivalent. However, the anthracite AC has a significantly larger surface area of the large pores. The Norit Ultra SX AC has slightly higher specific volumes of both micropores and macro pores.

Table 5.18: Surface Area and Pore Volume of Activated Carbon Catalyst Supports

	BET Surface Area (m ² /g)	Large-Pore Surface Area (m ² /g)	Micropore Volume < 2.0 nm (cm ³ /g)	Macropore Volume > 2.0 nm (cm ³ /g)
Norit SX Ultra	951	387	0.26	0.63
Anthracite AC	1075	742	0.14	0.5

5.8.1. Effect on catalyst activity

Figure 5.16 shows the average CO conversion of catalysts supported on the commercial AC (Norit ultra SX) and the in-house AC based on anthracite coal. The data reported in the figure correspond to time on stream between 24 and 48 h.

The baseline catalyst with anthracite AC supports shows better activity than with the commercial support. However, the 0% Fe catalyst supported on anthracite AC support and the 32%Fe catalyst supported on anthracite AC results in slight decreases in CO conversion relative to those of the catalysts supported on the commercial AC. For the case of no Mo and large Mo, the commercial AC showed better CO conversion. Changes with Cu loading are small for both cases, but the anthracite AC supported catalysts resulted in higher conversions at all values of Cu. The anthracite supported catalysts show better conversions at all values of K, on the other hand the commercial AC supported catalysts shows large changes in CO conversion with K loading.

Figure 5.16: Effect of Catalyst support on CO Conversion (300°C, 300psig, syngas flowrate 100sccm/min; 24-48 hours)

5.8.2 Effect on yields of Hydrocarbons and Alcohols

Figure 5.17 shows the effect of catalyst support on the yield of hydrocarbons and alcohols for catalysts with varying composition.

The baseline catalyst supported on anthracite AC produces more hydrocarbons and less alcohol relative to the baseline catalyst supported on the commercial AC, although the totals are approximately the same. On increasing the Fe loading, the yield of hydrocarbons and alcohols increases slightly for the catalyst supported on anthracite AC but there is a large increase in the yield of hydrocarbons for the catalysts supported on commercial AC. At high and low Mo loading, the catalysts supported on commercial AC is greater, especially for the yields of hydrocarbons. Further, the catalysts supported on anthracite AC the yield is higher for the high and low K loading, in particular the hydrocarbon production rate. Varying the Cu loading shows small changes for both cases, however the catalyst supported on anthracite AC with no Cu promotion shows higher yield of hydrocarbons.

Figure 5.17: Effect of Catalyst support on yield of hydrocarbons and alcohols (300°C, 300psig, syngas flowrate 100scm/min; 24-48 hours)

Chapter 6

Conclusions and Future Work

6.1 Conclusions

Based on the various runs performed in order to study the effect of the catalyst composition on the overall FTS activity in a fixed bed reactor at 300°C, 300 psig, 100 sccm/min, the following conclusions can be drawn:

1. The activated carbon support and the fresh baseline catalyst were characterized by BET, SEM/EDX and TPR. Surface area and pore volume were observed to decrease by 45% and 55% respectively with addition of metals on the support. EDX confirms relatively uniform coating of the metals on the support. TPR results suggest that all the phases of metal oxides get reduced slowly and simultaneously in a single step.
2. The stainless steel reactor alone and the activated carbon support alone (with no metals impregnated), were found to have minimal catalytic activity.
3. The baseline catalyst shows moderate catalytic activity and high CO₂ selectivity. Large amounts of hydrocarbons and small amounts of alcohols are formed. The CO₂ selectivity and the WGS activity are high.
4. Varying the Fe composition results in an increase in CO conversion. Also, CO₂ selectivity increases and the usage ratio decreases, hence the FT activity and the WGS activity increases when the Fe composition increases. The methane selectivity remains unchanged; however the C₂-C₄ selectivity decreases with increase in Fe loading. On increasing the Fe loading, the selectivity of higher molecular-weight hydrocarbons increases. Further the amount of Fe loading shows only a small effect on the yield of alcohols.

5. A small amount of potassium increases FTS activity, while larger amounts decrease FTS activity. This result is consistent with the findings of Ma et al.²⁸ using simpler catalysts (Fe/K and Fe/K/Cu catalysts). The 0% K catalyst shows the maximum CO₂ selectivity and least usage ratio indicating high water-gas shift activity. The selectivity of C₁-C₄ decreases with addition of K, and the selectivity of higher hydrocarbons increases with the addition of K. A small amount of potassium increases the formation of primary olefins, while a larger amount of potassium has a smaller effect. Further the yield of hydrocarbons does not change significantly with addition of a small amount of K, but decreases with addition of more K. But the alcohol production rate increases with an increase in potassium loading. These results were found to be consistent with the finding of Ma et al.²⁸
6. A small amount of Mo results in an increase in FTS activity but the activity decreases on addition of more Mo. The CO₂ selectivity increase with the increase in Mo loading. The C₂-C₄ hydrocarbon selectivity increases with the addition of a small amount of Mo, and decreases with addition of more Mo. The methane selectivity and C₅₊ hydrocarbon selectivity increase with increase in Mo content. Further, it was observed that Mo promoter improves alcohol selectivity. These results were found to be consistent with the findings of Ma et al.^{20, 28}
7. Varying the copper loading has very small effects on all parameters. For the three catalysts with varying Cu, the hydrocarbon production rate is high and about the same. The alcohol selectivity is less than 5 wt% for all the three catalysts. These results are consistent with the data reported by Ma et al.²⁸
8. Regression analysis is used to analyze the data statistically. The R² values of the regression models are very low. The models seem to be a poor fit for the data but are useful in indentifying the parameters to be optimized for formulation of mutli-component Fe-based catalysts.
9. Anthracite-based AC support shows better activity for the baseline catalyst, all values of K loading catalysts. On the other-hand, commercial AC support shows better activity for

the varying Mo catalysts and the 32% Fe loading catalyst produced double the yield of hydrocarbons. Changes with Cu loading for both the cases had small effects on the parameters, although the anthracite AC support shows higher activity.

6.2 Recommendations for Future Work

Based on the outcomes of this work, few recommendations for future work are mentioned in this section.

1. In this work, the activated carbon support and the baseline catalyst were characterized using the techniques mentioned in section 3.6. Similar analysis could be extended for the remaining catalysts with varying compositions of the metals.
2. The effect of varying reaction conditions (i.e. temperature, flowrate and pressure) should be investigated. Also, effect of amount of catalyst to be used should also be studied.
3. Further the stability studies should be performed.

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Appendices

Appendix A: Trace Element Analysis of Support

National Research Center for Coal and Energy
PO Box 6064, Evansdale Drive
Morgantown, WV 26506-
6064

phone 304-293-2867 ext. 5472

Client: Soumya Gujjar
Address:

Sample Date: 04/12/10
Sampled By: Client
Received in Lab: 04/12/10

Project: Activated carbon sample prepared from anthracite (after washing and drying @ 90°C overnight)

Analysis Completed: 6/2/2010

Analyte			Ag	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu
Method Number			200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Analysis Date			05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10
Method Detection Limit	Matrix	Lab ID	0.045	0.021	0.047	0.014	0.012	0.011	0.1	0.014	0.015	0.012	0.015
activated carbon sample	Solid	10'0144	31.17	2433.4	6.338	20.98	56.79	<0.011	357.84	0.814	3.57	18.69	16.85
Analyte			Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb
Method Number			200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7
			mg/kg	mg/kg	mg/kg	mg/kg	mg/L	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Analysis Date			05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10
Method Detection Limit	Matrix	Lab ID	0.013	0.100	0.100	0.017	0.050	0.100	0.019	0.047	0.032	0.047	0.035
activated carbon sample	Solid	10'0144	493.61	309.87	27.33	2.54	21.95	178.45	13.65	95.95	<0.032	4503.3	9.82
Analyte			Se	Si	Sn	Sr	Ti	Tl	V	Zn			
Method Number			200.7	200.7	200.7	200.7	200.7	200.7	200.7	200.7			
			mg/kg	mg/kg	mg/kg	mg/kg	mg/L	mg/kg	mg/kg	mg/kg			
Analysis Date			05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10	05/04/10			
Method Detection Limit	Matrix	Lab ID	0.045	0.050	0.039	0.011	0.014	0.040	0.011	0.016			
activated carbon sample	Solid	10'0144	26.46	571.64	6.76	45	109.22	<0.04	19.36	6.66			

Approved by:

Kenneth L. Stewart, Laboratory Director

Appendix B: Calculation Steps for Catalyst Preparation

Project

Catalyst Preparation

Notebook No.

Continued from Page

Support 4 g of AC (Anthracite coal based) - pore volume = 0.14 ml/gm
 $= 0.56 \text{ ml/4 g AC}$

Composition = 6 wt% Mo, 16 wt% Fe, 0.8 wt% Cu, 0.9 wt% K.

- (i) Mo = 6 wt% on AC = 0.24 g Mo on 4 g AC
 Molecular weight of Ammonium Molybdate = 1235.86 g/mol
 Molecular weight of Mo = 95.94 g/mol

$$\begin{array}{rcl} 1235.8 \text{ g salt} & \equiv & 95.94 \text{ g Mo} \\ ? \text{ g salt} & - & 0.24 \text{ g Mo} \\ \hline = \frac{0.24 \times 1235.8}{95.94} & = & \underline{0.44 \text{ g salt}} \end{array}$$

- (ii) Fe = 16 wt% on AC $\equiv$ 0.64 g Fe on 4 g AC

(Mol. wt)

$$\begin{array}{rcl} 404 \text{ g of Ferric Nitrate} & \text{contains} & = 55.845 \text{ g Fe} \\ ? & - & 0.64 \text{ g Fe} \\ \hline = \frac{404 \times 0.64}{55.845} & = & \underline{4.63 \text{ g Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}} \end{array}$$

- (iii) Cu = 0.8 wt% $\equiv$ 0.032 g Cu on 4 g AC.

Molecular weight of Cupric Nitrate = 232.6 g .

Mol. wt of Cu = 63.55 g .

$$\begin{array}{rcl} 232.6 \text{ g salt} & \equiv & 63.55 \text{ g Cu} \\ ? & - & 0.032 \text{ g Cu} \\ \hline = \frac{0.032 \times 232.6}{63.55} & = & \underline{0.117 \text{ g salt}} \end{array}$$

- (iv) K = 0.9 wt% $\equiv$ 0.036 g K on 4 g AC.

Mol. wt of Potassium Nitrate = 101.1 g/mol

Mol. wt of K = 39 g .

$$\begin{array}{rcl} 101.1 \text{ g salt} & \equiv & 39 \text{ g K} \\ ? & - & 0.036 \text{ g K} \\ \hline = \frac{0.036 \times 101.1}{39} & = & \underline{0.093 \text{ g salt}} \end{array}$$

Continued on Page

Gumya

Signed

04/08/2010

Date

Read and Understood By

Signed

Date

Appendix C: Mass-Flow Controller Calibration Curves

Figure C. 1: MFC calibration curve for He gas

Figure C. 2: MFC calibration curve for Hydrogen gas

Figure C. 3: MFC calibration curve for Syngas mixture (45%CO, 45%H₂, 5% Ar, 5%He)

Appendix D: Gas Chromatograph Operating Conditions

Gas chromatograph model: Perkin Elmer

Detector used: Thermal-conductivity detector (TCD)

Flame-ionization detector (FID)

Detector Temperature: TCD: 200°C

FID: 250°C

Carrier gas: He for TCD

N₂ for FID

Carrier gas inlet pressure: He: 33 psig

N₂: 14.1 psig

Carrier gas flowrate: He: 40ml/min

N₂: 30ml/min

Flowrate of H₂: 45ml/min

Flowrate of air: 450ml/min

Columns used: 18'' RGAP, 1/8" Sf; 17' RGA20, 1/8" Sf; 7' RGAP 1/8" Sf; 7" RGA, 1/8" Sf;
7' HayeSep N, 1/8" Sf; 9' Molecular Sieve, 13x1/8" Sf; 9' Molecular Sieve, 1/8"
Sf; 4' HayeSep T, 1/8" Sf.

Oven Temperature: 60°C

Period of analysis: 15 minutes

D.1.1 TCD calibration of gases

Relative response factor (rRF) is a measure of the response of the instrument detector to a target gas compared to an internal standard. Helium gas is used as the internal standard for helium, hydrogen, and carbon dioxide gas compounds. Argon gas is used as the internal standard for nitrogen, methane, and carbon monoxide gas compounds. The rRF can be calculated using the following equation

$$\text{relative Response Factor of gas component } X, (rRF)_X = \left(\frac{\frac{A_X}{C_X}}{\frac{A_{He,Ar}}{C_{He,Ar}}} \right) = \frac{slope_X}{slope_{He,Ar}} \quad \dots(D.1)$$

Where, A_X is the peak area of component and C_X is the concentration of component.

The rRF for standard is assumed to be 1. Different gases have different thermal conductivities and hence act differently on the TCD. To obtain an accurate quantification, rRF is used. Known quantities of a gas are sent into the GC along with known quantities of internal standard.

Table D. 1: Response Factor of TCD gas compounds

Component	rRF
H ₂	1.222
CO	0.951
He	1
Ar	1
N ₂	0.890
CO ₂	1.569
CH ₄	0.768

D.1.2 FID calibration of gases

Methane was used as the internal standard. The equation D.1 is used to calculate the rRF is modified as,

$$\text{relative Response Factor of gas component } X, (rRF)_X = \left(\frac{\frac{A_X}{C_X}}{\frac{A_{CH_4}}{C_{CH_4}}} \right) = \frac{slope_X}{slope_{CH_4}} \quad \dots (D.2)$$

The rRF of FID gas components are given in the Table D.2

Table D. 2: Response Factor of FID gas compounds

Compound	rRF
CH ₄	1
C ₂ H ₆	1.886
C ₂ H ₄	1.886
C ₃ H ₈	2.806
C ₃ H ₆	2.712
C ₃ H ₄	2.157
i-C ₄ H ₁₀	3.630
n-C ₄ H ₁₀	3.810
1-C ₄ H ₈	3.587
i-C ₄ H ₈	1.204
t-C ₄ H ₈	3.410
c-C ₄ H ₈	3.825
1,3 C ₄ H ₆	3.557
i-C ₅ H ₁₂	3.999
n-C ₅ H ₁₂	2.961
C ₅₊ gas	5.933

Appendix E: Chromatograph Operating Conditions for Liquid Products

Gas chromatograph model: Varian 3400GC equipped with Varian 8100 Autosampler's rack

Operating pressure of auto injector: 30 psig

Detector: Two Flame ionization detectors

Front Column: MXT 2887 capillary column with a 10m length, 0.53mm inner diameter and a 2.65 μ m film thickness

Back Column: Restek packed column, TX-TA 80/100, 6 ft length, 2mm ID, 1/8 in OD, SILCO
VAR 3400 PRECOND OC INV: 2in, OUTV: 1.5

Carrier Gas: Nitrogen for both columns

Carrier Gas inlet pressure: Column A: 6 psig

Column B: 82 psig

Table E. 1: GC Operating Conditions for liquid product analysis

	Column A operating conditions (oil phase analysis)	Column B operating conditions (aqueous phase analysis)
Column Conditions		
Initial column Temperature (°C)	50	50
Final column Temperature (°C)	300	340
Column initial hold time (min)	0	0
Column temperature rate (°C/min)	10	10
Detector Conditions		
FID Dectector	A	B
Temperature (°C)	300	300

	Column A operating conditions (oil phase analysis)	Column B operating conditions (aqueous phase analysis)
Injector Conditions		
Initial injection Temperature (°C)	200	200
Final injection Temperature (°C)	250	250
Injection hold time (min)	1	0
Injection temperature rate (°C/min)	10	10
Period of analysis (min)	48	28

E.1.1 Organic Liquid (Oil) Phase Products

CS₂ is used as the solvent for sample preparation. The straight-chain paraffins were identified by matching retention times of D-2887 quantitative calibration mix obtained from Restek. Branched paraffins, followed by olefins are assumed to elute before the straight-chain paraffin with the same carbon number. Also the response factors for all the liquid hydrocarbons are assumed to be linear and constant i.e. it is assumed the area percentage on the chromatogram is equal to the weight percentage of the sample.

E.1.2 Aqueous Phase Products

Cyclohexanol as an internal standard is used for aqueous phase preparation. First the retention times are identified using Accustandard calibration mix (PS-111 C Alcohols C₁-C₅ kit). Following this, each standard alcohol sample is added to known amount of Cyclohexanol and is injection in the GC. The areas are noted. The areas and weights of the components are tabulated in Table E.1.1. Using these values the aqueous compounds are quantified, the detailed procedure is discussed in Appendix F.2.

Table E.1. 1: Areas and Weights of Standard Alcohol Samples

Standard (x)	W _t _{cyclohexanol, standard} (μg)	W _t _{x, standard} (μg)	A _{x, standard}	A _{cyclohexanol, standard}
Methanol	22.2	383.7	84286	19451
Ethanol	18.3	225.6	82843	16693
2-Propanol	5.8	816.1	12534417	290032
1-Propanol	19.5	305.1	78959	16539
2-Butanol	34.2	796.5	31995228	1832669
1-Butanol	18.1	391.4	82482	18344
2-Pentanol	21	783.9	41499452	135882
1-Pentanol	18.8	388.3	77869	19888

Appendix F: Calculation Procedure for FTS Activity Results

F.1 Calculation procedure for Gas Analysis

F.1.1 TCD gas analysis

Helium gas is used as the internal standard for helium, hydrogen, and carbon dioxide gas compounds. Argon gas is used as the internal standard for nitrogen, methane, and carbon monoxide gas compounds. Feed flow (mol/min) is given by,

$$F_{X,out} \left(\frac{\text{mol}}{\text{min}} \right) = \frac{(A_{X,out})}{(A_{He,Ar,out}) \times (rRFx)} \times F_{He,Ar,in} \left(\frac{\text{mol}}{\text{min}} \right) \quad \dots\dots (F.1)$$

F.1.2 FID gas analysis

Outlet product flow rate is given by,

$$F_{X,out} \left(\frac{\text{mol}}{\text{min}} \right) = \frac{(A_{X,out})}{(A_{CH_4,out}) \times (rRFx)} \times F_{CH_4,out,TCD} \left(\frac{\text{mol}}{\text{min}} \right) \quad \dots\dots(F.2)$$

F.2 Calculation procedure for Liquid Analysis

F.2.1 Oil phase analysis

Assumption made: Linear and constant response factors. Hence, the weight percentage of the liquid hydrocarbons is calculated directly from GC areas.

$$\text{wt \% of liquid hydrocarbon, } x \text{ (wt}_x\text{ \%)} = 100 \times \frac{\text{Area of hydrocarbon, } x}{\text{Total area} - \text{Area of CS}_2} \quad \dots\dots(F.3)$$

$$\text{Actual weight of hydrocarbon, } x \text{ (gm)} = 100 \times \frac{\text{wt}_x\text{ \% of hydrocarbons}}{\text{weight of oil collected (gm)}} \quad \dots\dots(F.4)$$

F.2.2 Aqueous phase analysis

The internal standard is used to correct for sample volume variations. So we have to correct for sample volume variations by taking the ratio of all peak areas to the internal standard in both the sample and the standard. Since the internal standard has a known concentration in both the sample and the standard, it can be used to correct for variations. Since the concentrations of

alcohols responsible for the standard peaks are known, this comparison will allow you to calculate a concentration from the sample peak areas.

Let's pick Methanol as an example:

In order to relate the Area of Methanol in sample to the area of Methanol in the standard, we must first correct for sample variations to arrive at a corrected area of Methanol.

$$A_{\text{corr, C1-OH}} = A_{\text{C1-OH, sample}} \cdot \frac{A_{\text{cyclohexanol, standard}}}{A_{\text{cyclohexanol, sample}}} \cdot \frac{Wt_{\text{cyclohexanol, sample}}}{Wt_{\text{cyclohexanol, standard}}} \dots \text{(F.5)}$$

Now, we can calculate weight of methanol in GC vial from this corrected area of methanol

$$Wt_{\text{C1-OH}} = A_{\text{corr, C1-OH}} \cdot \frac{Wt_{\text{C1-OH, standard}}}{A_{\text{C1-OH, standard}}} \dots \text{(F.6)}$$

$A_{\text{C1-OH, standard}}$, $A_{\text{cyclohexanol, standard}}$, $Wt_{\text{cyclohexanol, standard}}$ (μg), $Wt_{\text{C1-OH, standard}}$ (μg) are provided in Table E.1. The subscript 'sample' in equation (F.5) refers to GC vial sample.

Similar procedure is followed for other alcohols and weights of alcohols can be calculated. Now we know the weights of all the alcohols (gm) in the GC vial. The weight of methanol in actual FT aqueous sample can be calculated as,

Methanol weight in Fischer-Tropsch aqueous sample

$$= \text{Weight of Aqueous weight collected in FT reaction (gm)} \times \frac{Wt_{\text{C1-OH, in GC vial}}}{\text{GC vial sample weight (gm)}} \dots \text{(F.7)}$$

GC vial sample weight (gm) is the sample weight in GC vial without cyclohexanol and water. Similarly, weight of other alcohols in Fischer-Tropsch aqueous sample can be calculated and sum of alcohols weight calculated in Fischer-Tropsch aqueous sample (gm) can be obtained.

Water amount in Fischer-Tropsch aqueous sample can be calculated as,

$$\text{Water in Fischer-Tropsch sample (gm)} = \text{Weight of Aqueous weight collected in FT reaction (gm)} - \text{sum of alcohols weight calculated in Fischer-Tropsch aqueous sample (gm)} \dots \text{(F.8)}$$

Appendix G: Ft Activity Data for Catalysts with Varying Fe Composition

G.1 Gas phase and oil phase analysis results

Table G. 1: Selectivity and Production rate of Hydrocarbons for Varying Fe Composition

Compound	0 % Fe		16%Fe		32% Fe	
	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day
C ₅₊	0	0	10.34	0.86	9.15	0.87
CH ₄	0	0	18.83	1.56	18.87	1.79
C ₂ H ₆ /C ₂ H ₄	0	0	18.58	1.54	15.60	1.48
C ₃ H ₈	0	0	7.17	0.59	5.67	0.54
C ₃ H ₆	0	0	15.35	1.27	15.16	1.44
i-C ₄ H ₁₀	0	0	0.21	0.02	0.17	0.02
C ₃ H ₄	0	0	0.00	0.00	0.00	0.00
n-C ₄ H ₁₀	0	0	2.68	0.22	2.65	0.25
1-C ₄ H ₉	0	0	2.50	0.21	3.61	0.34
i-C ₄ H ₈	0	0	2.71	0.22	2.48	0.24
t-C ₄ H ₉	0	0	4.20	0.35	3.38	0.32
c-C ₄ H ₉	0	0	3.07	0.25	2.78	0.26
1,3 C ₄ H ₆	0	0	0.00	0.00	0.00	0.00
i-C ₅ H ₁₂	0	0	0.01	0.00	0.03	0.00
n-C ₅ H ₁₂	0	0	2.30	0.19	2.33	0.22
C ₆	0	0	0.75	0.06	0.98	0.09
C ₇	0	0	1.06	0.09	2.26	0.21
C ₈	0	0	1.18	0.10	2.14	0.20
C ₉	0	0	1.07	0.09	2.03	0.19

Compound	0 % Fe		16%Fe		32% Fe	
	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day
C ₁₀	0	0	0.80	0.07	1.44	0.14
C ₁₁	0	0	0.62	0.05	0.99	0.09
C ₁₂	0	0	0.42	0.03	0.65	0.06
C ₁₃	0	0	0.23	0.02	0.45	0.04
C ₁₄	0	0	0.13	0.01	0.32	0.03
C ₁₅	0	0	0.06	0.00	0.23	0.02
C ₁₆	0	0	0.06	0.00	0.16	0.02
C ₁₇	0	0	0.04	0.00	0.12	0.01
C ₁₈	0	0	0.03	0.00	0.09	0.01
C ₁₉	0	0	0.02	0.00	0.06	0.01
C ₂₀	0	0	0.02	0.00	0.05	0.00
C ₂₁	0	0	0.02	0.00	0.04	0.00
C ₂₂	0	0	0.01	0.00	0.04	0.00
C ₂₃	0	0	0.01	0.00	0.03	0.00
C ₂₄	0	0	0.01	0.00	0.03	0.00
C ₂₅	0	0	0.01	0.00	0.16	0.02
C ₂₆	0	0	0.01	0.00	0.00	0.00
C ₂₇	0	0	0.01	0.00	0.00	0.00
C ₂₈	0	0	0.02	0.00	0.00	0.00
C ₂₉	0	0	0.02	0.00	0.00	0.00
C ₃₀	0	0	0.02	0.00	0.00	0.00
C ₃₁	0	0	0.02	0.00	0.00	0.00
C ₃₂	0	0	0.02	0.00	0.00	0.00

Compound	0 % Fe		16%Fe		32% Fe	
	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day
C ₃₃	0	0	0.02	0.00	0.00	0.00
C ₃₄	0	0	0.02	0.00	0.00	0.00
C ₃₅	0	0	0.01	0.00	0.00	0.00
iso-C ₇	0	0	0.12	0.01	0.34	0.03
iso-C ₈	0	0	0.29	0.02	0.42	0.04
iso-C ₉	0	0	0.12	0.01	0.52	0.05
iso-C ₁₀	0	0	0.61	0.05	0.41	0.04
C ₆ ole	0	0	0.02	0.00	0.97	0.09
C ₇ ole	0	0	0.22	0.02	0.82	0.08
C ₈ ole	0	0	0.45	0.04	0.33	0.03
C ₉ ole	0	0	1.15	0.10	0.41	0.04
C ₁₀ ole	0	0	0.45	0.04	0.33	0.03
C ₁₁ ole	0	0	0.60	0.05	0.54	0.05
C ₁₂ ole	0	0	0.40	0.03	0.19	0.02
C ₁₃ ole	0	0	0.24	0.02	0.23	0.02
C ₁₄ ole	0	0	0.09	0.01	0.15	0.01

G.2 Aqueous Phase Analysis

Table G. 2: Aqueous Phase results for Varying Fe Composition

Compound	0 % Fe		16%Fe		32% Fe	
	Weight (mg)	Alcohol in wt%	Weight (mg)	Alcohol in wt%	Weight (mg)	Alcohol in wt%
Methanol	0	0	33.8	8.44	84.0	3.25
Ethanol	0	0	77.1	19.26	181.3	7.02
2-Propanol	0	0	14.2	3.55	40.0	1.55
1-Propanol	0	0	19.8	4.94	80.5	3.12
2-Butanol	0	0	3.7	0.93	11.1	0.43
1-Butanol	0	0	20.4	5.11	41.5	1.61
2-Pentanol	0	0	0.1	0.03	0.3	0.01
1-Pentanol	0	0	3.3	0.83	12.8	0.50
Water	0	0	227.7	56.91	2130.3	82.51

Appendix H: Ft Activity Data for Catalysts With Varying Potassium Composition

H.1 Gas phase and Oil phase Analysis results

Table H. 1: Selectivity and Production rate of Hydrocarbons for Varying K Composition

Compound	0 % K		0.9 % K		1.8 % K	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₅₊	0.49	6.08	0.86	10.34	0.52	10.74
CH ₄	2.43	30.21	1.56	18.83	0.66	13.83
C ₂ H ₆ /C ₂ H ₄	1.84	22.85	1.54	18.58	0.69	14.32
C ₃ H ₈	1.25	15.57	0.59	7.17	0.14	2.82
C ₃ H ₆	0.54	6.75	1.27	15.35	0.96	19.94
i-C ₄ H ₁₀	0.03	0.33	0.02	0.21	0.01	0.22
C ₃ H ₄	0.00	0.00	0.00	0.00	0.00	0.00
n-C ₄ H ₁₀	0.40	4.93	0.22	2.68	0.12	2.47
1-C ₄ H ₉	0.08	1.01	0.21	2.50	0.30	6.25
i-C ₄ H ₈	0.14	1.79	0.22	2.71	0.02	0.45
t-C ₄ H ₉	0.21	2.59	0.35	4.20	0.15	3.16
c-C ₄ H ₉	0.14	1.74	0.25	3.07	0.14	2.85

Compound	0 % K		0.9 % K		1.8 % K	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
1,3 C ₄ H ₆	0.00	0.00	0.00	0.00	0.00	0.00
i-C ₅ H ₁₂	0.01	0.09	0.00	0.01	0.00	0.00
n-C ₅ H ₁₂	0.29	3.55	0.19	2.30	0.10	2.14
C ₆	0.02	0.20	0.06	0.75	0.08	1.73
C ₇	0.01	0.16	0.09	1.06	0.07	1.40
C ₈	0.02	0.20	0.10	1.18	0.09	1.78
C ₉	0.02	0.20	0.09	1.07	0.10	2.17
C ₁₀	0.02	0.21	0.07	0.80	0.09	1.79
C ₁₁	0.01	0.17	0.05	0.62	0.06	1.33
C ₁₂	0.01	0.13	0.03	0.42	0.05	0.99
C ₁₃	0.01	0.10	0.02	0.23	0.04	0.75
C ₁₄	0.01	0.08	0.01	0.13	0.03	0.58
C ₁₅	0.01	0.07	0.0049	0.06	0.02	0.45
C ₁₆	0.00	0.05	0.0049	0.06	0.02	0.31

Compound	0 % K		0.9 % K		1.8 % K	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₁₇	0.00	0.04	0.0035	0.04	0.01	0.25
C ₁₈	0.00	0.03	0.0026	0.03	0.01	0.22
C ₁₉	0.00	0.03	0.0020	0.02	0.01	0.17
C ₂₀	0.00	0.02	0.0016	0.02	0.01	0.14
C ₂₁	0.00	0.02	0.0013	0.02	0.01	0.12
C ₂₂	0.00	0.02	0.0011	0.01	0.00	0.10
C ₂₃	0.00	0.01	0.0010	0.01	0.00	0.08
C ₂₄	0.00	0.01	0.0009	0.01	0.00	0.07
C ₂₅	0.00	0.02	0.0008	0.01	0.00	0.06
C ₂₆	0.00	0.00	0.0008	0.01	0.00	0.05
C ₂₇	0.00	0.00	0.0009	0.01	0.01	0.24
C ₂₈	0.00	0.00	0.0013	0.02	0.00	0.00
C ₂₉	0.00	0.00	0.0016	0.02	0.00	0.00
C ₃₀	0.00	0.00	0.0019	0.02	0.00	0.00

Compound	0 % K		0.9 % K		1.8 % K	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₃₁	0.00	0.00	0.0018	0.02	0.00	0.00
C ₃₂	0.00	0.00	0.0016	0.02	0.00	0.00
C ₃₃	0.00	0.00	0.0013	0.02	0.00	0.00
C ₃₄	0.00	0.00	0.0013	0.02	0.00	0.00
C ₃₅	0.00	0.00	0.0012	0.01	0.00	0.00
iso-C ₇	0.00	0.05	0.01	0.12	0.46	0.46
iso-C ₈	0.00	0.04	0.02	0.29	0.32	0.46
iso-C ₉	0.01	0.10	0.01	0.12	0.77	0.46
iso-C ₁₀	0.00	0.00	0.05	0.61	0.49	0.46
C ₆ ole	0.01	0.08	0.00	0.02	0.79	0.46
C ₇ ole	0.01	0.16	0.02	0.22	1.30	0.46
C ₈ ole	0.00	0.05	0.04	0.45	0.45	0.46
C ₉ ole	0.00	0.03	0.10	1.15	0.29	0.46
C ₁₀ ole	0.01	0.09	0.04	0.45	0.21	0.46

Compound	0 % K		0.9 % K		1.8 % K	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₁₁ ole	0.01	0.07	0.05	0.60	0.42	0.46
C ₁₂ ole	0.00	0.04	0.03	0.40	0.24	0.46
C ₁₃ ole	0.00	0.03	0.02	0.24	0.17	0.46
C ₁₄ ole	0.00	0.00	0.01	0.09	0.11	0.46

H.2 Aqueous phase Analysis results

Table H. 2: Aqueous Phase results for Varying K Composition

Compound	0 % K		0.9 % K		1.8 % K	
	Weight (mg)	Alcohol wt%	Weight (mg)	Alcohol wt%	Weight (mg)	Alcohol wt%
Methanol	55.9769542	4.80	33.8	8.44	67.5	4.50
Ethanol	66.31105345	5.69	77.1	19.26	154.1	10.27
2-Propanol	9.523781432	0.82	14.2	3.55	28.4	1.89
1-Propanol	29.04751081	2.49	19.8	4.94	39.5	2.63
2-Butanol	2.195433203	0.19	3.7	0.93	7.4	0.49
1-Butanol	15.4232638	1.32	20.4	5.11	40.9	2.73
2-Pentanol	0.049149313	0.00	0.1	0.03	0.2	0.01
1-Pentanol	5.745934394	0.49	3.3	0.83	6.6	0.44
Water	980.7269194	84.18	227.7	56.91	1155.3	77.02

Appendix I: Ft Activity Data for Catalysts With Varying Molybdenum Composition

I.1 Gas phase and Oil phase Analysis results

Table I. 1: Selectivity and Production rate of Hydrocarbons for Varying Mo Composition

Compound	0 % Mo		6 % Mo		12% Mo	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₅₊	0.00	0.00	0.86	10.34	0.20	12.68
CH ₄	0.00	0.00	1.56	18.83	0.35	22.41
C ₂ H ₆ /C ₂ H ₄	0.00	0.00	1.54	18.58	0.27	17.67
C ₃ H ₈	0.00	0.00	0.59	7.17	0.10	6.32
C ₃ H ₆	0.00	0.00	1.27	15.35	0.21	13.44
i-C ₄ H ₁₀	0.00	0.00	0.02	0.21	0.00	0.00
C ₃ H ₄	0.00	0.00	0.00	0.00	0.00	0.00
n-C ₄ H ₁₀	0.00	0.00	0.22	2.68	0.04	2.39
1-C ₄ H ₉	0.00	0.00	0.21	2.50	0.03	1.73
i-C ₄ H ₈	0.00	0.00	0.22	2.71	0.00	0.00
t-C ₄ H ₉	0.00	0.00	0.35	4.20	0.06	3.88
c-C ₄ H ₉	0.00	0.00	0.25	3.07	0.04	2.47

Compound	0 % Mo		6 % Mo		12% Mo	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
1,3 C ₄ H ₆	0.00	0.00	0.00	0.00	0.00	0.00
i-C ₅ H ₁₂	0.00	0.00	0.00	0.01	0.00	47.91
n-C ₅ H ₁₂	0.00	0.00	0.19	2.30	0.00	0.00
C ₆	0.00	0.00	0.06	0.75	0.00	0.15
C ₇	0.00	0.00	0.09	1.06	0.02	1.32
C ₈	0.00	0.00	0.10	1.18	0.02	1.07
C ₉	0.00	0.00	0.09	1.07	0.02	1.34
C ₁₀	0.00	0.00	0.07	0.80	0.02	1.35
C ₁₁	0.00	0.00	0.05	0.62	0.02	1.42
C ₁₂	0.00	0.00	0.03	0.42	0.02	1.12
C ₁₃	0.00	0.00	0.02	0.23	0.01	0.85
C ₁₄	0.00	0.00	0.01	0.13	0.01	0.66
C ₁₅	0.00	0.00	0.0049	0.06	0.01	0.55
C ₁₆	0.00	0.00	0.0049	0.06	0.01	0.45

Compound	0 % Mo		6 % Mo		12% Mo	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₁₇	0.00	0.00	0.0035	0.04	0.01	0.36
C ₁₈	0.00	0.00	0.0026	0.03	0.0042	0.27
C ₁₉	0.00	0.00	0.0020	0.02	0.0036	0.23
C ₂₀	0.00	0.00	0.0016	0.02	0.0029	0.19
C ₂₁	0.00	0.00	0.0013	0.02	0.0023	0.15
C ₂₂	0.00	0.00	0.0011	0.01	0.0020	0.13
C ₂₃	0.00	0.00	0.0010	0.01	0.0017	0.11
C ₂₄	0.00	0.00	0.0009	0.01	0.0015	0.10
C ₂₅	0.00	0.00	0.0008	0.01	0.0015	0.09
C ₂₆	0.00	0.00	0.0008	0.01	0.00	0.00
C ₂₇	0.00	0.00	0.0009	0.01	0.00	0.00
C ₂₈	0.00	0.00	0.0013	0.02	0.00	0.00
C ₂₉	0.00	0.00	0.0016	0.02	0.00	0.00
C ₃₀	0.00	0.00	0.0019	0.02	0.00	0.00

Compound	0 % Mo		6 % Mo		12% Mo	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₃₁	0.00	0.00	0.0018	0.02	0.00	0.00
C ₃₂	0.00	0.00	0.0016	0.02	0.00	0.00
C ₃₃	0.00	0.00	0.0013	0.02	0.00	0.00
C ₃₄	0.00	0.00	0.0013	0.02	0.00	0.00
C ₃₅	0.00	0.00	0.0012	0.01	0.00	0.00
iso-C ₇	0.00	0.00	0.01	0.12	0.0047	0.3067
iso-C ₈	0.00	0.00	0.02	0.29	0.0037	0.2369
iso-C ₉	0.00	0.00	0.01	0.12	0.0105	0.6800
iso-C ₁₀	0.00	0.00	0.05	0.61	0.00	0.00
C ₆ ole	0.00	0.00	0.00	0.02	0.0086	0.5584
C ₇ ole	0.00	0.00	0.02	0.22	0.0162	1.0516
C ₈ ole	0.00	0.00	0.04	0.45	0.0055	0.3547
C ₉ ole	0.00	0.00	0.10	1.15	0.0035	0.2272
C ₁₀ ole	0.00	0.00	0.04	0.45	0.0097	0.6275

Compound	0 % Mo		6 % Mo		12% Mo	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₁₁ ole	0.00	0.00	0.05	0.60	0.0068	0.4427
C ₁₂ ole	0.00	0.00	0.03	0.40	0.0042	0.2691
C ₁₃ ole	0.00	0.00	0.02	0.24	0.0029	0.1847
C ₁₄ ole	0.00	0.00	0.01	0.09	0.0000	0.0000

I.2 Aqueous Phase analysis data:

Table I. 2: Aqueous Phase results for Varying Mo Composition

Compound	0 % Mo		6 % Mo		12 % Mo	
	Weight (mg)	Alcohol wt%	Weight (mg)	Alcohol wt%	Weight (mg)	Alcohol wt%
Methanol	0	0.00	33.8	8.44	24.0	4.00
Ethanol	0	0.00	77.1	19.26	28.5	4.74
2-Propanol	0	0.00	14.2	3.55	4.1	0.68
1-Propanol	0	0.00	19.8	4.94	12.5	2.08
2-Butanol	0	0.00	3.7	0.93	0.9	0.16
1-Butanol	0	0.00	20.4	5.11	6.6	1.10
2-Pentanol	0	0.00	0.1	0.03	0.0	0.00
1-Pentanol	0	0.00	3.3	0.83	2.5	0.41
Water	0	0.00	227.7	56.91	520.9	86.82

Appendix J: Ft Activity Data for Catalysts With Varying Copper Composition

J.1 Gas and Oil phase analysis

Table J. 1: Selectivity and Production rate of Hydrocarbons for Varying Cu Composition

Compound	0 % Cu		0.8 % Cu		1.6 % Cu	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₅₊	0.82	12.30	0.86	10.34	0.78	11.05
CH ₄	1.07	16.01	1.56	18.83	1.41	19.95
C ₂ H ₆ /C ₂ H ₄	1.02	15.27	1.54	18.58	1.31	18.50
C ₃ H ₈	0.35	5.20	0.59	7.17	0.50	7.09
C ₃ H ₆	1.09	16.39	1.27	15.35	1.20	16.99
i-C ₄ H ₁₀	0.01	0.21	0.02	0.21	0.01	0.21
C ₃ H ₄	0.00	0.00	0.00	0.00	0.00	0.00
n-C ₄ H ₁₀	0.17	2.48	0.22	2.68	0.21	2.93
1-C ₄ H ₉	0.22	3.37	0.21	2.50	0.23	3.21
i-C ₄ H ₈	0.17	2.60	0.22	2.71	0.20	2.83
t-C ₄ H ₉	0.28	4.21	0.35	4.20	0.32	4.46
c-C ₄ H ₉	0.22	3.28	0.25	3.07	0.24	3.38
1,3 C ₄ H ₆	0.00	0.00	0.00	0.00	0.00	0.00
i-C ₅ H ₁₂	0.00	53.00	0.00	0.01	0.00	59.58
n-C ₅ H ₁₂	0.00	0.00	0.19	2.30	0.00	0.00
C ₆	0.16	2.34	0.06	0.75	0.19	2.64
C ₇	0.08	1.24	0.09	1.06	0.04	0.53
C ₈	0.07	1.01	0.10	1.18	0.03	0.43

Compound	0 % Cu		0.8 % Cu		1.6 % Cu	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₉	0.08	1.26	0.09	1.07	0.04	0.54
C ₁₀	0.08	1.27	0.07	0.80	0.04	0.54
C ₁₁	0.09	1.33	0.05	0.62	0.04	0.57
C ₁₂	0.07	1.06	0.03	0.42	0.03	0.45
C ₁₃	0.05	0.80	0.02	0.23	0.02	0.34
C ₁₄	0.04	0.62	0.01	0.13	0.02	0.26
C ₁₅	0.03	0.52	0.0049	0.06	0.02	0.22
C ₁₆	0.03	0.43	0.0049	0.06	0.01	0.18
C ₁₇	0.02	0.34	0.0035	0.04	0.01	0.14
C ₁₈	0.02	0.25	0.0026	0.03	0.01	0.11
C ₁₉	0.01	0.22	0.0020	0.02	0.01	0.09
C ₂₀	0.01	0.18	0.0016	0.02	0.01	0.07
C ₂₁	0.01	0.14	0.0013	0.02	0.0042	0.06
C ₂₂	0.01	0.12	0.0011	0.01	0.0036	0.05
C ₂₃	0.01	0.10	0.0010	0.01	0.0031	0.04
C ₂₄	0.01	0.09	0.0009	0.01	0.0028	0.04
C ₂₅	0.01	0.09	0.0008	0.01	0.0027	0.04
C ₂₆	0.01	0.08	0.0008	0.01	0.0046	0.06
C ₂₇	0.0047	0.07	0.0009	0.01	0.01	0.12
C ₂₈	0.0041	0.06	0.0013	0.02	0.00	0.00
C ₂₉	0.0032	0.05	0.0016	0.02	0.00	0.00

Compound	0 % Cu		0.8 % Cu		1.6 % Cu	
	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%	gHC/day	Selectivity,wt%
C ₃₀	0.0022	0.03	0.0019	0.02	0.00	0.00
C ₃₁	0.0018	0.03	0.0018	0.02	0.00	0.00
C ₃₂	0.00	0.00	0.0016	0.02	0.00	0.00
C ₃₃	0.00	0.00	0.0013	0.02	0.00	0.00
C ₃₄	0.00	0.00	0.0013	0.02	0.00	0.00
C ₃₅	0.00	0.00	0.0012	0.01	0.00	0.00
iso-C ₇	0.02	0.29	0.01	0.12	0.0087	0.1236
iso-C ₈	0.01	0.22	0.02	0.29	0.0067	0.0955
iso-C ₉	0.04	0.64	0.01	0.12	0.0194	0.2740
iso-C ₁₀	0.04	0.53	0.05	0.61	0.0159	0.2250
C ₆ ole	0.07	0.99	0.00	0.02	0.0300	0.4237
C ₇ ole	0.02	0.33	0.02	0.22	0.0101	0.1429
C ₈ ole	0.01	0.21	0.04	0.45	0.0065	0.0915
C ₉ ole	0.04	0.59	0.10	1.15	0.0179	0.2528
C ₁₀ ole	0.00	0.00	0.04	0.45	0.00	0.00
C ₁₁ ole	0.03	0.42	0.05	0.60	0.0126	0.1784
C ₁₂ ole	0.02	0.25	0.03	0.40	0.0077	0.1084
C ₁₃ ole	0.01	0.17	0.02	0.24	0.0053	0.0744
C ₁₄ ole	0.01	0.12	0.01	0.09	0.0000	0.0000

J.2 Aqueous Phase analysis results:

Table J. 2: Aqueous Phase results for Varying Cu Composition

Compound	0 % Cu		0.8 % Cu		1.6 % Cu	
	Weight (mg)	Alcohol wt%	Weight (mg)	Alcohol wt%	Weight (mg)	Alcohol wt%
Methanol	55.37	4.46	33.8	8.4	46.2	4.20
Ethanol	108.16	8.71	77.1	19.3	88.5	8.04
2-Propanol	20.36	1.64	14.2	3.6	17.9	1.62
1-Propanol	54.36	4.38	19.8	4.9	40.7	3.70
2-Butanol	5.17	0.42	3.7	0.9	4.3	0.39
1-Butanol	15.80	1.27	20.4	5.1	12.5	1.14
2-Pentanol	0.12	0.01	0.1	0.0	0.1	0.01
1-Pentanol	12.31	0.99	3.3	0.8	8.9	0.81
Water	970.35	78.13	227.7	56.9	881.0	80.09

**Fischer-Tropsch Synthesis for Kerosene-Range Products Using a Multi-Component
Catalyst Supported on Coal-Based Activated Carbon**

Soumya Gujjar

**Thesis submitted to the College of Engineering and Mineral Resources at
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for the degree of**

Master of Science in Chemical Engineering

Department of Chemical Engineering

APPROVAL OF THE EXAMINING COMMITTEE

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