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Tailoring Multi-component Catalysts on Carbon Supports for Fischer-Tropsch Products in the Kerosene Range

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Tailoring Multi-component Catalysts on Carbon Supports for Fischer-Tropsch Products in the Kerosene Range

Joshua B Welshans

Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of

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in
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ABSTRACT

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Joshua B Welshans

The effects of varying the loading of four promoters on activated carbon supported iron catalysts were investigated. The base case catalyst studied consists of 6 wt% Mo, 16 wt% Fe, 0.8 wt% Cu and 0.9 wt% K. Molybdenum loadings of 0 wt%, 3 wt%, 6 wt% and 12 wt% were studied along with iron loadings of 0 wt%, 8 wt%, 16 wt% and 32%, copper loadings of 0 wt%, 0.4 wt%, 0.8 wt% and 1.6 wt%, and potassium loadings of 0 wt%, 0.45 wt%, 0.9 wt% and 1.8 wt%. The reactor conditions used were 300°C, 300 psig, and 6 NL/gcat/h. The syngas used had a H₂/CO ratio of 1.0. The reaction was carried out over a period of 72 hours.

Data were gathered on the gaseous products and the two phases of the liquid products, the aqueous phase (containing oxygenates such as alcohols) and the oil phase (containing hydrocarbons such as paraffins and olefins). The data reported in this thesis were taken from the 24-48 hour period. The data gathered were fitted in a regression model. Catalysts were characterized using BET, XRD and TPR. Results were also compared to similar studies, but with simpler catalyst formulations.

The addition of Mo lowers CO conversion, but increases stability. The oxygenate production has a maximum at 6% Mo. An increase in Mo loading corresponds to a decrease in oil production. An increase in Fe loading causes an increase in CO conversion. Changes in the Fe loading do not significantly effect aqueous production. Increases in Fe content causes an increase in oil production. Changes in Cu loading have little effect on all parameters. The absence of K in the catalyst causes a very low conversion while all other K catalysts have comparable CO conversions. Increasing the K loading causes an increase in oil production.

Equations for the CO conversion, oil fraction yield, hydrocarbon production rate, olefin-to-paraffin ratio, gasoline range production and diesel range production were fitted. The oil fraction yield and olefin-to-paraffin ratio equations were very good fits to the data while the other equations did not fit the data as well.

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Chapter 1

Introduction

Fischer-Tropsch synthesis (FTS) is a catalytic process defined as “a hydrogenation of oxides of carbon producing much higher hydrocarbons or alcohols.”¹

The main reactions pertinent to FTS are the hydrocarbon polymerization reaction

and the water gas shift reaction (WGS).

In 1902, the first reports of heterogeneous CO hydrogenation on Ni catalysts yielding methane were made by scientists Sabatier and Senderens. BASF has patents from 1913 reporting the synthesis of liquid hydrocarbons using Co on Os catalysts. The products consisted of paraffins, olefins and oxygenates (i.e. alcohols, ethers). These studies led to the development of the first methanol synthesis plant that went on stream in 1923².

The Fischer-Tropsch process as known today was invented in the 1920s by German scientists Franz Fischer and Hans Tropsch. Their classic experiments date back to 1922, where they used high pressure and temperatures with alkalized iron catalysts to perform CO hydrogenation².

Until 1945, FTS was carried out in 15 plants in countries such as Germany, France, Japan and China. After World War II, most of these plants were dismantled and those that were still operational had to be shut down for economic reasons². Currently, the process is commercially used by a limited number of companies in few locations such as Sasol in South Africa and Shell in Malaysia.

The largest implementation of FTS technology comes from Sasol. Sasol is a South African company with a series of plants along with a large stake in plants owned by other companies such as the Oryx Gas-to-Liquid (GTL) plant in Qatar. These plants produce gasoline and diesel from coal and natural gas. Sasol uses cobalt-based catalysts in their processes.

Rentech operates a demonstration-scale plant in the United States. The facility is designed to produce over 400 gallons per day of synthetic jet fuel, aviation fuel, diesel, and specialty waxes and chemicals. The plant can utilize biomass, coal, and natural gas for its feedstock. Rentech also has a number of full-scale plants in the design phase. The company uses iron-based catalysts.

A major challenge in the way of feasibility of large scale commercial FTS plants is economics. To be economic, the process needs a high selectivity to diesel and gasoline based on the syngas used, due to its cost accounting for roughly 80% of production costs³.

The purpose of this project was to develop a catalyst for FTS to produce a single battlefield fuel using materials obtainable in the United States, namely iron and activated carbon (AC). For this project, catalysts containing Mo, Fe, Cu and K on activated carbon supports were investigated. The catalyst composition that was used as a base case consisted of 6 wt% Mo, 16 wt% Fe, 0.8 wt% Cu and 0.9 wt% K. A systematic approach was used to test the effectiveness of various catalyst compositions. The parameter of interest was the yield of total hydrocarbons in the range of C₉ to C₁₅, the gasoline/kerosene range. Oxygenates were also of interest.

The reaction conditions were not varied for this study and were 300°C, 300 psig and 6 NL/gcat/h. The syngas used had a ratio of 1.0 (H₂/CO). The goal of this project was

to study the effects of varying the four elemental composition variables. Parameters that were of interest include selectivity, activity and stability.

Chapter 2

Literature Review

2.1 Fischer-Tropsch Catalysts

2.1.1 Catalysts

Group VIII metals are commonly used as Fischer-Tropsch catalysts. The activity of the Group VIII metals were determined and reported as Ru, Fe, Co, Rh, Pd, Pt, and Ir in order of decreasing activity⁴. Iron is often used due to its low cost. Table 2.1 shows a relative comparison in cost of some commonly used FTS catalysts.

Table 2.1: Relative Prices of Common FTS Catalyst metals⁵	
Metal	Price Ratio (circa 1989)
Iron	1
Cobalt	230
Nickel	250
Ruthenium	31,000
Rhodium	570,000

In addition to the low cost, the advantages of iron catalysts are high activity for FTS and WGS⁵. Iron catalysts have a high selectivity toward olefins³. Undesirable effects of iron catalysts include oxidation, carburization of the reduced metal or deposition of elemental carbon⁶. Oxidation results in a loss of active surface area as iron oxides are inactive for FTS⁷. Catalysts particle swelling can be caused by elemental carbon deposition which could result in the plugging of fixed bed reactors⁷.

Cobalt catalysts are viable for producing middle distillate (kerosene, diesel) FTS products using natural gas as the feedstock. When converting natural gas to syngas, a H₂:CO ratio of 2+ is seen⁸. This works well for cobalt catalysts because of their low WGS activity⁸. Because there is an abundance of H₂ already in the feedstock, WGS is not

needed to produce H_2 for the reaction. The products from a cobalt-catalyzed FTS are generally saturated long-chain hydrocarbons or higher linear alcohols⁹.

Ni, Rh and Ru are not very viable choices for FTS. Ni has a very high selectivity toward methane while Ru and Rh are very expensive and not widely available⁵.

2.1.2 Promoters

The addition of promoters to Co and Ru catalysts does not affect the efficiency very much. With Co, the addition of thorium and alkali promoters increases the wax production, and supports are used to increase the surface area of the active metal. In contrast, promoters are essential for iron catalysts².

Mo has been shown¹⁰ to increase Fe catalyst stability in small amounts (6%); however, in large amounts (12%), it decreases the yield of higher numbered hydrocarbons.

Copper has been shown¹¹ to promote the FTS reaction in Fe catalysts. The reaction rate increases with the addition of a small amount (0-2%) of Cu¹¹. It also increases the rate of the WGS, but not the CO_2 selectivity¹¹. Methane selectivity decreases while heavier product selectivity increases with the amount of Cu¹¹. Cu does not have any effect on alkene selectivity¹¹. The addition of Cu also leads to an increased rate of reduction, thereby allowing it to be carried out at lower temperatures².

The hydrogenation activity of iron catalysts is largely influenced by the addition of “electronic promoters” such as alkali metals. Their efficiency depends on the basicity and the following order is found: Rb, K, Na, and Li, from best to worst². With the addition of electronic promoters, an increase in activity and an enhanced selectivity toward CO-consuming reactions is seen². This means that the average molecular weight

of the products is increased, methane formation is decreased, olefin formation is increased, and oxygenated product formation is increased². Small amounts of potassium have been shown¹² to increase catalytic activity while increasing potassium decreases activity and increases the deactivation rate of the catalyst.

Alkaline promoters lead to a decrease in the active surface area of iron catalysts. Structural promoters are added in order to compensate for this effect. These consist of nonreducible metal oxides such as Al_2O_3 and Cr_2O_3 . These give high surface areas, but slow the rate of reduction².

2.1.3 Catalyst Pretreatment

In order to become active for FTS, catalysts must be activated through a pretreatment process. When iron oxides are activated under hydrogen, they form metallic iron¹³. This is subsequently converted to iron carbides when syngas is introduced¹³. The active phase for iron is thought to be iron carbides¹⁴. Pretreatment of Fe catalysts is not as simple as it is in cobalt catalysts where the active phase is thought to be Co metal.

Table 2.2 shows the change in the degree of reduction of an iron catalyst with different gases. The reduction conditions were 673K at 8 hours with a fixed space velocity. When CO is used in the reduction gas, the degree of reduction is much less than that of a catalyst reduced by only H_2 . However, iron carbides are only present in catalysts reduced with CO. Studies done by Luo and Davis¹⁴ indicate that the highest conversions (60-80%) are obtained by CO-activated catalysts while the lowest conversions (40-60%) are from H_2 -activated catalysts. This is consistent with iron carbides being the active phase for Fe-based FT catalysts.

Table 2.2: Degree of Reduction Using Different Gases¹⁴		
Gas	Reduction (%)	Phases Present
100% H ₂	80	α -Fe, Fe ₃ O ₄
98% H ₂ + 2% CO	20	Fe ₅ C, Fe ₃ O ₄
100% CO	4	Fe ₅ C, Fe ₃ O ₄

2.1.4 Catalyst Poisoning

There are two types of poisoning: reversible and irreversible. Reversible poisoning is caused by compounds containing oxygen such as O₂, CO, and H₂O, while irreversible poisoning is attributed to non-metals such as sulfur, chlorine and phosphorus¹⁵.

Iron, cobalt, and nickel catalysts are rapidly deactivated by all sulfur-containing compounds². It has been explained² that sulfur deactivates the catalyst by withdrawing electrons from the catalyst surface. This is said¹⁶ to be due to the suppression of electron back-bonding. Sulfur has also been shown² to inhibit the dissociation of CO. Fortunately, the efficiency of modern-day gas purification systems can reduce the sulfur level in syngas to tolerable levels², below 0.03mg/m³.

Iron catalysts which have been poisoned by sulfur cannot be readily reactivated. Only very thorough reoxidation, where all traces of sulfur are burnt away, followed by reduction, is effective².

Chloride and bromide ions are also known to deactivate iron catalysts². There are two mechanisms suggested for chlorine poisoning of iron catalysts¹⁵. One involves the formation of iron-chlorine compounds which could increase the size of the iron crystallites¹⁵. As a result, the active surface area of the catalyst will decrease. The other possible mechanism has the chlorine interacting with potassium, an important promoter in iron catalysts, forming KCl¹⁵. The KCl could diffuse into the catalyst grain or diffuse

into the gas stream, causing an irreversible loss of potassium¹⁵ and consequent loss of activity.

2.2 Selectivity

The products from FTS can vary with varying operating conditions and with the type of catalyst used. Anderson¹ describes some pertinent characteristics of the FTS products, based mostly on data from cobalt and iron catalysts:

1. Water is a primary product due to WGS. Primary alcohols and α -olefins may also be primary products.
2. The carbon number distribution on a molar basis is large for C_1 , then drops for C_2 , increases to a local maximum for either C_3 or C_4 , and then decreases monotonically.
3. Monomethyl-substituted hydrocarbons are present in moderate amounts.
4. Dimethyl species are present in significantly smaller amounts than monomethyl species. Ethyl-substituted species are found in similar amounts to dimethyl species.
5. Using iron catalysts, naphthenes and aromatics are produced in small amounts in fixed-bed reactors, while moderate amounts are found in fluidized reactors. None of these products are usually produced with a cobalt catalyst.
6. Olefins produced from iron catalysts are often found in amounts exceeding 50% of each carbon number, and more than 60% of these are α -olefins. These fractions are independent of carbon number. With a cobalt catalyst, these fractions are smaller and decrease with increasing carbon number.

7. Alcohol yields are a maximum at C₂ and decrease monotonically with higher carbon number.

2.2.1 The Anderson-Schulz-Flory Distribution

The Anderson-Schulz-Flory (ASF) distribution gives the chain length distribution if the hydrocarbon chain is formed step-wise by insertion or addition of C₁ intermediates with a constant chain growth probability (α)¹⁷, which is the probability that a molecule will continue reacting to form a longer chain rather than begin a new chain. The ASF equation is as follows:

$$\log\left(\frac{W_n}{n}\right) = n \log \alpha + \log(\ln^2 \alpha) \quad (2.1)$$

where W_n is the mass fraction of the species with carbon number n. This means that W_n/n can be plotted in semi-log coordinates against n to yield a straight line whose slope is log α .

Figure 2.1 shows the weight fraction as a function of the chain growth probability for varying n as calculated with Equation 2.1:

Figure 2.1: Example of the Weight Fraction as a Function of the Chain Growth Probability Factor as Calculated by the ASF Equation

2.2.2 Deviations from the ASF Distribution

In most cases deviations from the ideal ASF distribution occur. The majority of reported ASF diagrams show a straight line only between C_4 - C_{12} . Methane tends to be more than predicted for Co and Ru catalysts. This is attributed to methyl groups being cleaved from 1-olefins. The C_2 and C_3 products are much less than predicted for Co and Ru catalysts, while only slightly less than predicted for Fe catalysts. This is thought to be because the ethane and propane are being incorporated into an olefin and initializing a new chain¹⁸.

The “two-site model” was developed by Koenig and Gaube¹⁹ for cases when a curved ASF diagram is obtained. This has happened in the case of an alkali-promoted

iron catalyst. It was hypothesized that the alkalization creates a second catalytic site. In these cases, the product distribution can be estimated by the superposition of two ASF diagrams, and two α values are obtained. A second, equivalent method was developed later by Stenger²⁰ and called the “distributed site model”. The assumption of this model is that the two sites are distributed randomly throughout the catalyst with concentration values between 0 and a maximum¹⁸.

Puskas and Hurlbut¹⁸ have reported that the ASF equations are fundamentally correct. Deviations from the ASF equations can be justified with kinetic considerations and accounting for secondary reactions.

2.3 Related WVU Laboratory Work

Recently, Ma^{10,12,21,22} worked extensively on this subject. In particular, the effect of activated carbon support source²¹, Mo loading¹⁰, K loading¹⁸, and Cu loading²² were investigated.

There has been a growing interest in AC as a catalyst support in recent years²¹. This is partially due to its low cost, unique texture and surface properties. The physical texture of AC has been reported to impact the reduction and dispersion of active metals on the support surface, especially when using the incipient-wetness impregnation technique. In addition, AC has been found to be a promising choice for restricting hydrocarbon chain length²¹. Studies involving iron, cobalt and molybdenum-nickel catalysts indicate that chain length could be limited to less than C₃₅ on AC²¹.

Ma²¹ investigated four different sources for the activated carbon support: peat, pecan, walnut, and a generic wood source. Table 2.3 summarizes the physical properties of the investigated sources in both unimpregnated and impregnated forms.

Supports and Catalysts	Total SA (m ² /g)	Mircopore SA (m ² /g)	Total PV (cm ³ /g)	Micropore volume (cm ³ /g)	Mean Pore Size (nm)	Percentage of Micropores (SA)	Percentage of Micropores (PV)
Peat Support	606	151	0.48	0.255	5.9	25	53
Wood Support	970	56	0.58	0.138	6.6	6	25
Pecan Support	1016	280	0.72	0.358	5.1	28	50
Walnut Support	892	233	0.50	0.182	3.9	26	37
Peat Catalyst	347	104	0.25	0.131	4.1	30	52
Wood Catalyst	534	52	0.32	0.084	5.4	10	25
Pecan Catalyst	499	89	0.32	0.122	4.0	18	38
Walnut Catalyst	476	54	0.29	0.081	3.7	11	28

The highest value for the BET total surface area belongs to the pecan-based AC support, and the peat-based has the lowest value. The pecan-based, walnut-based and peat-based AC supports have wide pores contributing 25-28% of the surface area while the wood-based only has 6% of the surface in wide pores. This suggests that all four supports are highly microporous.

Once impregnated with the metals, both total surface area and total pore volume decrease by nearly the same amount. When taking only the wide pores into consideration, the pecan-based and walnut-based catalysts have the largest decrease in surface area (~73%), the peat-based catalyst has a significantly smaller decrease (31%), while the wood-based catalyst has the smallest decrease (~9%). The same trend is seen in pore volume, with a 61% decrease in the pecan-based and walnut-based catalysts, a 49% decrease in the peat-based catalyst, and a 39% decrease in the wood-based catalyst.

Table 2.4 contains information on the reaction studies with the four ACs.

Table 2.4: Reaction Results for Catalysts of Differing Activated Carbon Supports ²¹				
AC Support	CO Conversion (%)	Selectivity (wt %)		
		C ₁	C ₂ -C ₄	C ₅₊
Peat	87.1	10.9	40.9	48.2
Wood	37.9	13.9	54.8	31.3
Pecan	90.1	15.3	32.4	52.3
Walnut	58.5	14.9	34.6	50.5

Catalysts with pecan- and peat-based AC supports have the highest CO conversion, while the wood-based catalysts have the lowest. The catalysts with the pecan-, walnut- and peat-based AC supports have the highest selectivity toward C₅₊ while the wood-based catalyst has a high selectivity toward C₂-C₄.

In investigating the effects of Mo loading, Ma¹⁰ made catalysts containing 0, 6 and 12 wt% Mo in addition to 15.7% Fe, 0.8% Cu, and 0.9% K. For the catalyst without Mo, the initial CO conversion is nearly 100%; however, the catalyst rapidly deactivates and the reaction was stopped after 72 hours. For the catalyst containing 6% Mo, the opposite effect is seen. The initial conversion is seen to be 60%, and it increases rapidly to 90% during the first 72 hours and remains stable for an additional 72 hours. In the case of the 12% Mo catalyst, the conversion starts out at 60%, the same as the 6% loading, but it then slowly decreases to 53% over a 143-hour period.

The percentage loading of Mo also changes the product distribution. Mo increases the amount of methane and inhibits the formation of higher molecular weight species. The selectivity of oxygenates is very low for all three loading percentages, but increases somewhat with loading.

Ma¹² also looked at the effects of potassium loading. For this, the catalysts prepared did not contain any other promoter. The amount of Fe used in all the catalysts

was 15.7% and potassium was used in the amounts of 0, 0.9 and 2%. In this study, the effect of temperature was also studied from 260-300°C, in 10°C increments. Briefly, the results of the study show that small amounts of potassium increase FTS activity while larger amounts hinder activity, and the potassium reduces catalyst stability. The potassium has a significantly larger effect on the extent of WGS than on FTS. At lower temperatures, the selectivity of C₁-C₄ products decreases while C₅₊ products increase with the addition of K. As the temperature is increased, the selectivity toward lower carbon numbers increases.

The effect of Cu loading was studied by Ma²². These catalysts did not contain Mo. The amount of Fe used in all catalysts was 15.7% and the amount of K was 0.9%. The amount of Cu used was 0, 0.8 and 2%. The effect of temperature were studied from 260-290°C. The addition of Cu significantly decreases reduction temperature and increases reduction rate. The addition of 0.8%Cu causes a decrease in both FTS and WGS activity; however, with the addition of 2%Cu, this change is lessened. The addition of Cu does not significantly change the overall hydrocarbon distribution. The addition of Cu leads to an increase in oxygenate selectivity.

Chapter 3

Experimental Equipment and Procedure

3.1 Materials

The activated carbon used for the catalyst support in this project is Norit SX Ultra procured from Sigma Aldrich. This AC was chosen due to its high surface area and pore volume, in addition to its recommendation by Norit for catalyst applications. Table 3.1 includes information on the AC obtained through BET analysis completed in the lab.

Table 3.1: Norit SX Ultra Properties Measured by BET			
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)
951	387	0.26	0.63

For the catalyst impregnation, the sources of Mo, Fe, Cu and K metals were (NH₄)₆Mo₇O₂₄·4H₂O, Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·2.5H₂O and KNO₃ respectively. All these chemicals were acquired from Sigma Aldrich. Section 3.3.1 contains the catalyst preparation procedure.

The gas cylinders that were used in the reactor system and the gas chromatographs were all purchased from Airgas. The description for the gas cylinders is included in Table 3.2.

Table 3.2: Gas Cylinder Types	
Gas	Purity
Syngas*	N/A
Air	Breathing Quality
Nitrogen	Ultra High
Helium	Ultra High
Hydrogen	Ultra High

*A mixture of 45% H₂, 45% CO, 5% He and 5% Ar

3.2 Equipment

3.2.1 Reactor System

A schematic of the reactor system is shown in Figure 3.1. There are three gas cylinders connected to the reactor system: helium, hydrogen and syngas (45% H₂, 45% CO, 5% He, 5% Ar). These gases are fed into separate mass flow controllers (MFCs) controlled by the computer. After the MFCs, the streams converge and enter the reactor. The reactor is a simple fixed-bed stainless-steel tube jacketed in a furnace. The furnace is regulated by the computer in the same program as the MFCs. Thermocouples are placed into the top of the reactor as well as on the outside of the reactor to record the temperature of the system. Figure 3.2 shows the catalyst bed in more detail. The procedure for loading the reactor is given later.

After the reactor, there is a liquid trap. This is shown in more detail in Figure 3.3. For this, a dip-leg is used to take the reactor effluent to the bottom of the trap. The liquid collects here, while the gas is free to flow around the dip-leg to a side stream that goes to the gas chromatograph (GC) and the vent. The valve at the bottom of the liquid trap is used to drain the liquid product for collection. The liquid trap is wrapped in copper tubing which has cooling water pumped through it. It was kept at a temperature between 5-10°C.

The reactor temperature and flowrate are controlled by a computer system running the program Wonderware. The pressure of the system is controlled through a back-pressure regulator.

Figure 3.1: Reactor Set-up

Figure 3.2: Schematic of the Catalyst Bed

Figure 3.3: Schematic of the Liquid Trap

3.2.2 Analysis of Reactor Outlet

Analysis of the gas product is handled by a Clarus 500 Gas Chromatograph (GC) from Arnel, Inc. The GC uses a dual Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID). The TCD notes difference in thermal conductivity between the carrier gas and the reactor effluent. The reason that a dual TCD is essential is due to the need to analyze for H_2 . The most common and sensitive inert carrier gas for the TCD is He; however, the thermal conductivities of He and H_2 are nearly identical, so H_2 cannot

be detected using He as a carrier gas. To detect H₂, a second TCD is utilized that employs N₂ as the carrier gas.

The FID is most efficient for analyzing organic compounds such as hydrocarbons, and uses hydrogen and air to light a flame. The temperature of this flame is able to pyrolyze most organic compounds, producing positive ions and electrons. These ions are detected by two electrodes, creating a potential difference that allows the organics to be detected.

Analysis of the liquid product is handled by a Varian 3400 GC. This GC is equipped with two FIDs. The FIDs are on two separate analytical columns. The two columns are used separately to analyze the two liquid phases, oil and aqueous, independently on separate FID channels. The oil phase is analyzed using an MXT 2887 capillary column with a 10m length, 0.53mm inner diameter and a 2.65µm film thickness. The aqueous phase is analyzed using a TXTA packed column that is 2m long and has a 2mm inner diameter.

3.2.3 Catalyst Characterization

The catalysts were characterized both pre- and post-reaction by Brunauer-Emmet-Teller (BET) surface area, X-ray diffraction (XRD), temperature-programmed reduction (TPR), CO chemisorption and energy-dispersive X-ray spectroscopy (EDS).

The BET technique uses liquid nitrogen to measure the adsorption of AC samples. From this, a series of equations in BET theory can be used to calculate the surface area. BET Theory is an extension of a monolayer molecular adsorption model, Langmuir theory, to a multilayer model. The equation used to determine the total surface area of the sample is:

$$S_{TOTAL} = \frac{v_m N s}{V} \quad (3.1)$$

where S_{TOTAL} is the total surface area, v_m is the volume of N_2 adsorbed in a monolayer, N is Avogadro's number, s is the adsorption cross-section (the amount that can be adsorbed into a cross-section), and V is the molar volume of the adsorbed species. A specific surface area (units of area/mass) can also be found using

$$S = \frac{S_{TOTAL}}{a} \quad (3.2)$$

where a is the mass of the absorbent. Surface area and pore volume measurements were made with a Micromeritics ASAP 2020.

XRD uses X-ray diffraction to find the crystalline structure and physical properties of materials. The scattering intensity of an X-ray beam is measured as a function of incident and scattered angles, polarization and wavelength. Crystals exhibit a unique diffraction pattern; with a mixture of crystals, the patterns appear independently of each other. These patterns can be used to identify the samples. This will give an idea of the phase of the metals in the catalyst (i.e. Fe metal, FeO, or Fe_3O_4). X-ray diffraction measurements were made using a PANalytical X'Pert PRO.

TPR is used to find the degree of reduction of the catalyst. A U-tube is filled with catalyst, and the air is removed using flowing inert gas. Hydrogen is added by mass flow controllers and a temperature program is initiated. The exit gas is analyzed by the appropriate detectors. When reduction takes place, hydrogen is consumed by the reaction and the change in hydrogen content of the exit stream is picked up by the detectors. Using the amount of hydrogen consumed, the degree of reduction (DR_T) can be calculated:

$$DR_T = \left(\frac{\text{Experimental H}_2 \text{ Consumed}}{\text{Theoretical H}_2 \text{ Required}} \right) \bullet 100 \quad (3.3)$$

EDS is used for elemental characterization of a sample. The sample is hit with an electron beam and releases X-rays in response. This is called X-ray fluorescence. Each element emits X-rays at characteristic energies which can be used to identify the elements present. The intensity of the fluorescence peaks can be used to discern the relative amounts of the elements present. The EDS being used is connected to a Hitachi S-4700 scanning electron microscope and is manufactured by EDAX/Ametek.

3.3 Experimental Procedure

3.3.1 Catalyst Synthesis

Activated carbon (AC) from Sigma-Aldrich was used as the catalyst support. The AC was washed by boiling it in deionized water, and the AC is dried. The first metal salt is then dissolved in water and added dropwise to the AC to incipient wetness. The order in which the salts were added to the carbon was as follows: Mo, Fe, Cu, and K. This is in the order of highest to lowest molecular weight of the compounds being used and was used by Ma^{10,12}. The amount of each metal salt used is shown in Table 3.3. After a salt was added to the AC, it was dried overnight in air at a temperature between 90°C and 100°C. Then the next salt could be added.

The base case composition is 6 wt% Mo, 16 wt% Fe, 0.8 wt% Cu and 0.9 wt% K. This composition is based on recent work done at WVU^{10,12}. Table 3.4 shows the composition of all catalysts produced and studied. Sample 1 is the base case catalyst, Samples 2-4 are variation in Mo, Samples 5-7 are variations in Fe, Samples 8-10 are variations in Cu and Samples 11-13 are variations in K.

Table 3.3: Amount of Metal Salt Added per gram AC		
Promoter	Composition (% Metal)	Amount of Salt (g/gAC)
Mo	0.0	0.000
	3.0	0.056
	6.0	0.111
	12.0	0.222
Fe	0.0	0.000
	8.0	0.579
	16.0	1.157
	32.0	2.314
Cu	0.0	0.000
	0.4	0.015
	0.8	0.029
	1.6	0.058
K	0.0	0.000
	0.45	0.024
	0.9	0.047
	1.8	0.094

Table 3.4 Catalyst Composition Breakdown				
	Component Percentage			
Sample	Mo	Fe	Cu	K
1	6.0	16.0	0.8	0.9
2	0.0	16.0	0.8	0.9
3	3.0	16.0	0.8	0.9
4	12.0	16.0	0.8	0.9
5	6.0	0.0	0.8	0.9
6	6.0	8.0	0.8	0.9
7	6.0	32.0	0.8	0.9
8	6.0	16.0	0.0	0.9
9	6.0	16.0	0.4	0.9
10	6.0	16.0	1.6	0.9
11	6.0	16.0	0.8	0.0
12	6.0	16.0	0.8	0.45
13	6.0	16.0	0.8	1.8

3.3.2 Reactor Procedure

Before loading the reactor, the position of the thermocouple in the reactor is measured and marked. Then ~1/16” quartz chips are added to the reactor, to guarantee that the thermocouple is in the catalyst bed. The catalyst/diluent mixture is added next.

This contains one gram of catalyst and four grams of $\sim 1/32''$ quartz chips, the same size as the catalyst particles, well mixed. A tuft of quartz wool is placed on either side of the catalyst mixture to ensure the catalyst bed does not move. Finally the reactor is topped off with $\sim 1/16''$ quartz chips. For a diagram of the reactor, refer to Figure 3.2.

Once the reactor is secured into the system, it is tested for leaks. When it is confirmed that there are no leaks, the pretreatment is begun. For this, the system is purged with helium and heated to 400°C . Hydrogen is then introduced to the system at 200 cc/min for 12 hours.

After pretreatment, the reactor is cooled to 300°C and pressurized to 300 psig with helium. The reaction is then started by introducing the syngas at a flowrate of 100 cc/min. The reaction proceeds for 72 hours, and then the system is shut down. For shutdown, the syngas flowrate is turned off and helium is once again flowed through the reactor until the reactor is cooled to room temperature. Once the reactor is cooled and the gas flows stopped, the reactor is disconnected from the system and the spent catalyst is collected for later characterization.

While the reaction is proceeding, the GC is set to take a sample from the effluent gas stream every hour. The gas-phase GC data are collected by a program called TotalChrom Workstation. This program automatically identifies and integrates the chromatogram's peaks. In order to calculate the amount of a gas phase component present, the response factor of that component must be acquired through calibration. In order to calibrate, known quantities of the gas to be calibrated are injected with varying amount of diluent. Comparing the amount injected with the response on the GC, the response factor can be calculated.

The liquid product is collected in 24-hour intervals. The liquid trap is emptied into a graduated cylinder and the volume is recorded. The weight is also measured with an electronic balance, by pouring the liquid into a pre-weighed vial. With the weight and volume recorded, the vial is labeled and stored in the refrigerator to minimize losses while awaiting further analysis. Liquid phase analysis is described in Section 3.3.3.

While each run produces three separate samples, one for each 24-hour period, only the second 24-hour period data are contained in the Results section, in the interest of consistency. The first 24-hour period is considered the startup period where the reaction is still coming to steady state, while the catalyst is considered to be deactivating during the final 24-hour period. This is a typical assumption in laboratory studies such as these.

3.3.3 Liquid Product Analysis Procedure

The liquid produced by the reaction is typically a two-phase mixture. The less-dense phase is the oil phase, containing mostly paraffins and olefins. The more-dense phase is the aqueous phase, containing mostly water and alcohols. These two phases are separated before a proper analysis of composition can be begun.

For the oil phase, a sample of the oil, typically 0.1 mL, is mixed with typically 0.9 mL of CS₂. CS₂ was chosen as the solvent because it has a very short retention time and a very low response on the FID.

Once the sample is prepared, the vial, along with any other vial to be tested, is placed into the Varian 8100 Autosampler rack. The GC is then started. The temperature program consists of an initial temperature of 50°C with a ramping of 10°C/min up to a final temperature of 300°C.

The program used to collect the data is the Varian Star Control System. This program automatically integrates any peaks detected; however, the peaks are not identified. The peaks were identified through the use of a calibration mixture. A calibration mixture consists of eight to ten hydrocarbons in the C₁-C₄₀ range at varying concentrations. This gives retention times for the included compounds, and the rest can be determined by inspection.

When calculating the amount of each component in the sample, the assumption is that, for paraffins and olefins, the area percentage on the chromatogram is equal to the weight percentage of the sample.

The aqueous-phase analysis is handled with an internal standard since water is not detected by the column in the GC. The internal standard was chosen to be cyclohexanol. Cyclohexanol was chosen because it was not a compound that would be produced by the FT reaction under normal circumstances, also its retention time was beyond those of the other compounds being detected.

A 1mL aliquot of the aqueous sample is transferred to a pre-weighed vial and this is weighed. Then approximately 20μL of cyclohexanol is added to the sample and the weight is recorded. From these numbers, the sample weight and cyclohexanol weight is determined.

These aqueous-phase samples are analyzed by the Varian Autosampler and GC in the same manner as the oil-phase samples described earlier, except that the final temperature in the program is 340°C rather than 300°C. Since there are relatively few alcohol species to be identified, the calibration mixture consists of a single pure alcohol (methanol, ethanol, etc.) mixed with approximately 20μL of cyclohexanol. The retention

time of the injected component is noted, along with the areas of the component and cyclohexanol.

In order to calculate the amount of each component in the sample, the areas and weights determined from the calibration are used. The corrected area for the component of interest is obtained from:

$$A_{corr,i} = A_{i,sample} \cdot \frac{A_{cyclohexanol,standard}}{A_{cyclohexanol,sample}} \cdot \frac{Wt_{cyclohexanol,sample}}{Wt_{cyclohexanol,standard}} \quad (3.4)$$

After obtaining the corrected area, the weight of the compound in the sample can be found from:

$$Wt_i = A_{corr,i} \cdot \frac{Wt_{i,standard}}{A_{i,standard}} \quad (3.5)$$

This calculation is repeated for all the oxygenates in the sample. Once all the oxygenate weights have been determined, the weight of water in the aqueous sample can be found by difference.

3.4. Safety

The reactant carbon monoxide is flammable in air at concentrations of 12.5% to 74.0%. There is also a danger from inhaling the gas, as it binds to the hemoglobin in blood and can greatly reduce the blood's ability to transport oxygen in the body. The permissible exposure limit set by OSHA is 50ppm time-weighted average (TWA, the amount a worker can be exposed to over the course of a work day). The material safety data sheet (MSDS) also lists it as a teratogen, a mutagen and a reproductive hazard. Teratogens interfere with normal embryonic development, and mutagens cause higher than normal genetic mutations to occur.

Hydrogen is also a flammable gas at concentrations between 4.0% and 74.5% in air. Hydrogen is not toxic, but will cause asphyxiation.

Neither helium nor nitrogen is flammable or toxic; however, they can cause asphyxiation.

In order to make sure no flammable gas is ignited in the course of the experiment, the reactor is purged with helium prior to each run. This ensures that there is no oxygen left (that could facilitate ignition) in the lines. Also, the reactor system is situated inside a large fume hood to protect personnel from the dangers of inhaling CO. Gas detectors are also wired to the system so that, in the event of a gas release, the system will shut itself down, preventing a larger volume of gas escaping.

To prevent a catastrophic failure due to a plug in the reactor causing a rapid increase in pressure, the reactor system is fitted with pressure relief valves.

Chapter 4

Results and Discussion

The catalysts described in Chapter 3 were prepared and tested in the reactor system of Figure 3.1. Each run was carried out under the same conditions: 300°C, 300psig, 6 NL/gcat/h syngas flowrate, with a 1:1 CO:H₂ ratio.

First the gas-phase results are discussed, followed by the liquid-phase results, for each catalyst promoter individually. Just as the liquid-phase data are based on the second 24-hour period, the gas-phase results are obtained using the hourly results from the second 24-hour period and averaging them.

Mass balance closures typically range $\pm 4\%$. Table 4.1 contains the mass balance closure data. A regression analysis of the data and characterization data are also included.

In the following tables, the catalysts will be referred to by the loading of the changing component only. The other components will have the same loading as the base case: 6%Mo, 16%Fe, 0.8%Cu and 0.9%K.

Table 4.1: Mass Balance Error	
Catalyst	Percent Error
6%Mo 16%Fe 0.8%Cu 0.9%K	-3.13
6%Mo 0%Fe 0.8%Cu 0.9%K	-1.36
6%Mo 8%Fe 0.8%Cu 0.9%K	-1.66
6%Mo 32%Fe 0.8%Cu 0.9%K	-3.52
0%Mo 16%Fe 0.8%Cu 0.9%K	-3.79
3%Mo 16%Fe 0.8%Cu 0.9%K	-3.13
12%Mo 16%Fe 0.8%Cu 0.9%K	-2.11
6%Mo 16%Fe 0%Cu 0.9%K	-3.91
6%Mo 16%Fe 0.4%Cu 0.9%K	-0.94
6%Mo 16%Fe 1.6%Cu 0.9%K	-0.31
6%Mo 16%Fe 0.8%Cu 0%K	-3.73
6%Mo 16%Fe 0.8%Cu 0.45%K	-4.31
6%Mo 16%Fe 0.8%Cu 1.8%K	-0.54

4.1 Effect of Varying Mo

The conversions for each Mo catalyst are shown in Figure 4.1. It can be seen that the reaction never get to steady state. The conversion for the 0%Mo catalyst starts off with the highest conversion; however, it deactivates quickly. The other Mo-containing catalysts show a higher stability. The 6%Mo catalyst shows higher conversion than the 3%Mo and 12%Mo catalysts, with the 12%Mo catalyst having the lowest conversion of all. Table 4.2 shows the average conversions for each catalyst during the 24-48 hour period. These results are consistent with those of Ma et al.¹⁰ using catalysts with Mo, Fe, Cu and K present.

Figure 4.1: CO Conversion Comparison for Iron Catalysts of Varying Mo Composition

Table 4.2: Average CO Conversion between 24-48 Hours for Varying Mo Catalysts	
Catalyst	Conversion (%)
0%Mo	42.5
3%Mo	19.1
6%Mo	28.5
12%Mo	11.4

The selectivities for the gas phase components are listed in Table 4.3. It can be seen that the addition of Mo causes a decrease in CO₂ production and an increase in CH₄ production. This is consistent with the findings of Ma et al¹⁰.

Table 4.3: Average Gas Phase Component Selectivities and Amounts (mmols/day) for Varying Mo Catalysts								
Compound	0%Mo		3%Mo		6%Mo		12%Mo	
	Select	Amount	Select	Amount	Select	Amount	Select	Amount
CO ₂	76.52	679	71.13	290	69.64	432	63.15	168
CH ₄	6.94	61.6	11.99	48.9	12.86	79.8	17.93	47.7
C ₂ H ₆ /C ₂ H ₄	5.73	50.9	5.81	23.7	6.14	38.1	6.95	18.5
C ₃ H ₈	0.54	4.80	1.07	4.35	1.17	7.27	1.29	3.43
C ₃ H ₆	4.75	42.1	4.17	17.0	4.45	27.6	5.07	13.5
i-C ₄ H ₁₀	0.06	0.54	0.03	0.12	0.04	0.24	0.00	0.00
n-C ₄ H ₁₀	0.31	2.73	0.58	2.38	0.62	3.84	0.62	1.64
1-C ₄ H ₈	2.30	20.4	1.49	6.08	1.34	8.32	1.00	2.66
i-C ₄ H ₈	0.27	2.43	0.00	0.00	0.00	0.00	0.00	0.00
trans-C ₄ H ₈	0.04	0.38	0.29	1.19	0.43	2.68	0.40	1.07
cis-C ₄ H ₈	0.06	0.50	0.34	1.37	0.48	3.00	0.41	1.08
1,3-C ₄ H ₆	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
i-C ₅ H ₁₂	0.03	0.27	0.00	0.00	0.00	0.00	0.00	0.00
n-C ₅ H ₁₂	0.24	2.16	0.54	2.21	0.57	3.51	0.52	1.39
C ₅₊	2.20	19.6	2.55	10.4	2.26	14.0	2.66	7.07

Appendix I contains the numbers for the aqueous products produced by Mo catalysts along with the base case. Table 4.4 shows a breakdown of the aqueous product masses. Figure 4.2 shows the selectivity for the five alcohol carbon numbers. For increasing Mo composition, the methanol production is increasing. The amount of ethanol produced decreases sharply with the addition of any Mo on the catalyst. These are both also seen in the study done by Ma¹⁰.

Amounts of individual compounds found in the oil fraction of the liquid phase produced by Mo catalysts are shown in detail in Appendix II. Table 4.5 contains information on the oil product lumped into three groups: C₆ through C₈, C₉ through C₁₅, and C₁₆₊. The reasoning is that this project focuses on producing diesel fuel which is in the C₉ to C₁₅ range. The 3%Mo has the largest percentage of oil produced in this range. Figure 4.3 shows the selectivities for each carbon number in the oil phase.

Compound	mmol			
	0%Mo	3%Mo	6%Mo	12%Mo
Methanol	1.13	2.77	8.20	4.72
Ethanol	2.89	4.77	11.25	4.05
2-Propanol	0.04	0.61	1.38	0.42
1-Propanol	0.87	1.28	4.38	1.11
2-Butanol	0.00	0.16	0.42	0.10
1-Butanol	0.51	1.60	2.64	0.83
2-Pentanol	0.00	0.01	0.01	0.00
1-Pentanol	0.20	0.88	1.20	0.40
Water	21.96	25.70	30.53	21.67

Figure 4.2: Alcohol Distribution for Catalysts of Varying Mo Content

Table 4.5 Lumped Oil Product Distribution for Varied Mo Catalysts			
Catalysts	Selectivity		
	C ₆ -C ₈	C ₉ -C ₁₅	C ₁₆ +
0%Mo	48.1	51.4	0.5
3%Mo	38.8	61.2	0.0
6%Mo	48.8	51.2	0.0
12%Mo	100	0.0	0.0

Figure 4.3: Oil Fraction Selectivity for Varying Mo

Table 4.6 contains broad properties of the total liquid products. Mo causes an increase in the total alcohol production up to 6%; at 12%, the total alcohol production falls off. This is consistent with the results of Ma et al¹⁰. Addition of Mo also causes a decrease in the total oil production as well as the olefin-to-paraffin ratio. This is inconsistent with the results of Ma et al who reported¹⁰ that the olefin-to-paraffin ratios are similar for all Mo catalysts. The addition of 12%Mo caused a drastic increase in oil production where the highest carbon number observed was 8. This is not consistent with

the results of Ma et al who reported an increase in higher molecular weight species with 12%Mo.

Catalyst	Total Alcohol Weight (mg)	Percent Alcohol in Water	Total Oil Weight (mg)	Highest Carbon Number	$\frac{Alcohols}{HCs}$ (%)	$\frac{Olefins}{Paraffins}$ (%)
0%Mo	279	41.4	3660	17	7.6	61.3
3%Mo	629	57.6	737	16	85.3	20.7
6%Mo	1460	72.6	675	20	216	15.1
12%Mo	534	57.8	440	8	121	0.0

4.2 Effect of Varying Fe

Figure 4.4 shows the results for CO conversion of the Fe catalysts. As can be expected, the general trend is that conversion increases with higher Fe content. Table 4.7 shows the average conversions for the 24-48 hour period. The effect of Fe loading was not studied by Ma.

Figure 4.4: CO Conversion Comparison for Iron Catalysts of Varying Fe Composition

Table 4.7: Average CO Conversion between 24-48 Hours for Varying Fe Catalysts	
Catalyst	Conversion (%)
0%Fe	1.8
8%Fe	24.9
16%Fe	28.5
32%Fe	54.4

Table 4.8 contains information on the average gas component selectivities. For the 0%Fe case, the reaction produces nothing more than small amounts of methane. The other Fe catalysts show a decreasing CO₂ production and increasing CH₄ production with higher Fe composition.

Table 4.8: Average Gas Phase Component Selectivities and Amounts (mmols) for Varying Fe Catalysts								
Compound	0%Fe		8%Fe		16%Fe		32%Fe	
	Select	Amount	Select	Amount	Select	Amount	Select	Amount
CO ₂	0.00	0.00	71.14	352	69.64	432	66.29	824
CH ₄	100	30.6	12.72	62.9	12.86	79.8	14.86	185
C ₂ H ₆ /C ₂ H ₄	0.00	0.00	5.60	27.7	6.14	38.1	6.54	81.3
C ₃ H ₈	0.00	0.00	1.51	7.46	1.17	7.27	1.76	21.9
C ₃ H ₆	0.00	0.00	3.65	18.0	4.45	27.6	4.26	52.9
i-C ₄ H ₁₀	0.00	0.00	0.04	0.21	0.04	0.24	0.05	0.63
n-C ₄ H ₁₀	0.00	0.00	0.72	3.57	0.62	3.84	0.84	10.5
1-C ₄ H ₈	0.00	0.00	0.87	4.31	1.34	8.32	1.02	12.6
i-C ₄ H ₈	0.00	0.00	0.25	1.25	0.00	0.00	0.30	3.67
trans-C ₄ H ₈	0.00	0.00	0.46	2.25	0.43	2.68	0.53	6.62
cis-C ₄ H ₈	0.00	0.00	0.49	2.40	0.48	3.00	0.57	7.05
1,3-C ₄ H ₆	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
i-C ₅ H ₁₂	0.00	0.00	0.05	0.23	0.00	0.00	0.06	0.69
n-C ₅ H ₁₂	0.00	0.00	0.64	3.17	0.57	3.51	0.75	9.29
C ₅ +	0.00	0.00	1.86	9.19	2.26	14.0	2.17	27.0

Appendix III contains data for the aqueous phase for Fe catalysts. Table 4.9 contains information on the masses of the aqueous phase components. Figure 4.5 includes information on the alcohol phase selectivities. As mentioned before, the 0%Fe catalyst produced no liquid product.

Table 4.9: Aqueous Product Amounts for Catalysts of Varying Fe				
Compound	mmol			
	0%Fe	8%Fe	16%Fe	32%Fe
Methanol	0.00	7.28	8.20	7.59
Ethanol	0.00	9.91	11.25	11.05
2-Propanol	0.00	0.98	1.38	1.53
1-Propanol	0.00	4.19	4.38	0.40
2-Butanol	0.00	0.26	0.42	0.40
1-Butanol	0.00	1.76	2.64	2.29
2-Pentanol	0.00	0.01	0.01	0.01
1-Pentanol	0.00	0.72	1.20	1.57
Water	0.00	26.37	30.53	56.80

Figure 4.5: Alcohol Distribution for Catalysts of Varying Fe Content

Amounts of individual compounds found in the oil fraction of the liquid phase are shown in detail in Appendix IV. Table 4.10 contains the percentages for the lumped oil product distribution. The 8%Fe catalyst produced the largest percentage of C₉-C₁₅ hydrocarbons. Figure 4.6 shows the selectivity for the oil fraction by carbon number

Table 4.10: Lumped Oil Product Distribution for Varied Mo Catalysts			
Catalysts	Selectivity		
	C ₆ -C ₈	C ₉ -C ₁₅	C ₁₆ +
0%Fe	0.0	0.0	0.0
8%Fe	36.2	60.6	3.2
16%Fe	48.8	51.2	0.0
32%Fe	46.8	51.7	1.5

Figure 4.6: Oil Fraction Selectivity for Varying Fe

An overview of the total liquid properties collected for the Fe catalysts is contained in Table 4.11. The 0%Fe catalyst performs expectedly, producing no liquid product. The oil production increases with Fe loading, while the alcohol production stays roughly constant.

Table 4.11: Liquid Product Properties for Catalysts of Varying Fe Composition						
Catalyst	Total Alcohol Weight (mg)	Percent Alcohol in Water	Total Oil Weight (mg)	Highest Carbon Number	$\frac{\text{Alcohols}}{\text{HCs}}$ (%)	$\frac{\text{Olefins}}{\text{Paraffins}}$ (%)
0%Fe	0	0.0	0	0	0.0	0.0
8%Fe	1215	71.9	550	17	220	23.1
16%Fe	1460	72.6	675	20	216	15.1
32%Fe	1207	54.1	1570	20	76.9	18.5

4.3 Effect of Varying Cu

Figure 4.7 shows the conversion data for the Cu catalysts. The change in Cu composition does not affect the conversion is a large way. Table 4.12 shows the average conversion between the period of 24-48 hours. The change in average conversion is on the order of $\pm 6\%$. Ma et al reported²², using catalysts containing only Fe, Cu and K, that the conversion decreased with the addition of Cu. However, the change from 0.8%Cu to 2%Cu did not affect the conversion significantly.

Figure 4.7: CO Conversion Comparison for Iron Catalysts of Varying Cu Composition

Table 4.12: Average CO Conversion between 24-48 Hours for Varying Cu Catalysts	
Catalyst	Conversion (%)
0%Cu	34.2
0.4%Cu	29.2
0.8%Cu	28.5
1.6%Cu	33.4

The selectivities for the gas phase components are listed in Table 4.13. Just as the conversions were not changed in any significant way, the gas selectivities were very similar between catalysts. This is consistent with Ma et al²². For the simpler catalysts studied by Ma, the production of CO and CH₄ were similar across all catalysts.

Table 4.13: Average Gas Phase Component Selectivities and Amounts (mmols) for Varying Cu Catalysts								
Compound	0%Cu		0.4%Cu		0.8%Cu		1.6%Cu	
	Select	Amount	Select	Amount	Select	Amount	Select	Amount
CO ₂	69.86	516	68.05	494	69.64	432	72.74	505
CH ₄	12.52	92.5	13.10	95.1	12.86	79.8	14.84	103
C ₂ H ₆ /C ₂ H ₄	6.01	44.4	7.80	56.6	6.14	38.1	5.82	40.4
C ₃ H ₈	1.37	10.2	1.21	8.78	1.17	7.27	2.87	19.9
C ₃ H ₆	4.27	31.6	4.21	30.6	4.45	27.6	0.93	6.43
i-C ₄ H ₁₀	0.04	0.32	0.05	0.36	0.04	0.24	0.07	0.50
n-C ₄ H ₁₀	0.69	5.09	0.61	4.43	0.62	3.84	0.96	6.67
1-C ₄ H ₈	1.19	8.65	1.11	8.06	1.34	8.32	0.08	0.54
i-C ₄ H ₈	0.04	0.30	0.00	0.00	0.00	0.00	0.00	0.00
trans-C ₄ H ₈	0.50	3.71	0.45	3.27	0.43	2.68	0.16	1.14
cis-C ₄ H ₈	0.53	3.93	0.55	3.99	0.48	3.00	0.04	0.26
1,3-C ₄ H ₆	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
i-C ₅ H ₁₂	0.01	0.06	0.00	0.00	0.00	0.00	0.00	0.00
n-C ₅ H ₁₂	0.62	4.60	0.65	4.72	0.57	3.51	0.63	4.35
C ₅₊	2.35	17.3	2.21	16.0	2.26	14.0	0.86	5.97

The data for Cu catalyst alcohol products is contained in Appendix V. The breakdown of the alcohol products is contained in Table 4.14 and Figure 4.8. Ma et al reported²² that the change in Cu loading did not affect the alcohol selectivities significantly. This is seen in most cases; however, there is an uncharacteristically large amount of 1-pentanol being produced for the 0%Cu catalyst. This is likely due to an error in the GC analysis.

Table 4.14: Aqueous Product Amounts for Catalysts of Varying Cu				
Compound	mmol			
	0% Cu	0.4% Cu	0.8% Cu	1.6% Cu
Methanol	4.90	6.98	8.20	3.46
Ethanol	6.42	8.27	11.25	4.21
2-Propanol	1.08	1.09	1.38	0.59
1-Propanol	2.45	2.09	4.38	1.15
2-Butanol	0.24	0.20	0.42	0.15
1-Butanol	1.92	1.54	2.64	1.05
2-Pentanol	0.00	0.00	0.01	0.00
1-Pentanol	4.16	0.51	1.20	0.55
Water	14.35	21.07	30.53	9.46

Figure 4.8: Alcohol Distribution for Catalysts of Varying Cu Content

Amounts of individual compounds found in the oil fraction of the liquid phase can be found in Appendix VI. Table 4.15 contains information on the lumped oil product distribution for the Cu catalysts. These numbers were not significantly affected by a change in Cu loading. This is consistent with the data reported by Ma et al²². Figure 4.9 contains selectivities for the oil phase according to carbon number.

Table 4.15: Lumped Oil Product Distribution for Varied Cu Catalysts			
Catalysts	Selectivity		
	C ₆ -C ₈	C ₉ -C ₁₅	C ₁₆ +
0%Cu	40.9	55.2	0.7
0.4%Cu	38.0	58.6	3.4
0.8%Cu	48.8	51.2	0.0
1.6%Cu	47.2	50.0	2.6

Figure 4.9: Oil Fraction Selectivity for Varying Cu

The total liquid product properties overview is shown in Table 4.16. The oil products produced are comparable across all catalysts along with the olefin-to-paraffin ratio. Ma et al²² also reported similar olefin-to-paraffin ratios across all of the studied catalysts. The 0.8%Cu catalyst produced the highest amount of alcohol product.

Table 4.16: Liquid Product Properties for Catalysts of Varying Cu Composition						
Catalyst	Total Alcohol Weight (mg)	Percent Alcohol in Water	Total Oil Weight (mg)	Highest Carbon Number	$\frac{\text{Alcohols}}{\text{HCs}}$ (%)	$\frac{\text{Olefins}}{\text{Paraffins}}$ (%)
0%Cu	1192	88.3	900	18	132	18.5
0.4%Cu	970	71.9	950	19	102	18.2
0.8%Cu	1460	72.6	675	20	216	15.1
1.6%Cu	547	76.3	970	18	56.4	15.3

4.4 Effect of Varying K

Figure 4.10 shows the CO conversion for the catalysts studied. The conversion for the 0%K catalyst is very low compared to the other catalysts; however, the conversions for K greater than 0.45% are comparable. Table 4.17 shows the average conversion between 24-48 hours. This is consistent with data reported by Ma et al¹² using simpler catalysts. Ma reported that small amounts of K can increase FTS activity while a large amount will decrease activity.

The selectivities of the gas phase components are contained in Table 4.18. For these, the CO₂ selectivity rises significantly with increasing K loading while the CH₄ selectivity decreases. This is consistent with data reported by Ma et al¹² using catalysts containing only Fe and K.

Figure 4.10: CO Conversion Comparison for Iron Catalysts of Varying K Composition

Table 4.17: Average CO Conversion between 24-48 Hours for Varying K Catalysts	
Catalyst	Conversion (%)
0%K	8.2
0.45%K	22.3
0.9%K	28.5
1.8%K	22.8

Table 4.18: Average Gas Phase Component Selectivities and Amounts (mmols) for Varying K Catalysts								
Compound	0% K		0.45% K		0.9% K		1.8% K	
	Select	Amount	Select	Amount	Select	Amount	Select	Amount
CO ₂	43.5	94.6	60.6	305	69.64	432	82.0	352
CH ₄	30.6	66.6	18.4	92.8	12.86	79.8	7.90	34.0
C ₂ H ₆ /C ₂ H ₄	12.1	26.3	7.57	38.2	6.14	38.1	3.99	17.2
C ₃ H ₈	5.98	13.0	2.58	13.0	1.17	7.27	0.45	1.95
C ₃ H ₆	1.92	4.17	4.10	20.7	4.45	27.6	2.50	10.8
i-C ₄ H ₁₀	0.15	0.33	0.06	0.30	0.04	0.24	0.00	0.00
n-C ₄ H ₁₀	2.00	4.34	1.09	5.51	0.62	3.84	0.24	1.01
1-C ₄ H ₈	0.16	0.35	0.64	3.23	1.34	8.32	1.29	5.52
i-C ₄ H ₈	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trans-C ₄ H ₈	0.34	0.74	0.80	4.05	0.43	2.68	0.00	0.00
cis-C ₄ H ₈	0.08	0.17	0.66	3.32	0.48	3.00	0.00	0.00
1,3-C ₄ H ₆	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
i-C ₅ H ₁₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-C ₅ H ₁₂	1.30	2.83	0.97	4.88	0.57	3.51	0.01	0.03
C ₅₊	1.79	3.88	2.51	12.6	2.26	14.0	1.63	7.00

Appendix VII contains alcohol data for K catalysts. Table 4.19 and Figure 4.11 show more information on the alcohol phase of the liquid products. The 0%K catalyst is the only catalyst to produce more methanol than ethanol. For the 0.9%K (base) catalyst, methanol production decreases while C₃₊ alcohol production increases in relation to the other K catalysts. This is inconsistent with results reported by Ma¹² as he produced oxygenates with all studied catalysts. It is possible that the higher K content in the 1.8%K catalyst caused a higher WGS rate causing no water to be collected and the aqueous product was left undetectable in the gas- or oil-phase.

Table 4.19: Aqueous Product Amounts for Catalysts of Varying K				
Compound	mmol			
	0% K	0.45% K	0.9% K	1.8% K
Methanol	3.89	1.42	8.20	0.00
Ethanol	1.75	1.09	11.25	0.00
2-Propanol	0.05	0.09	1.38	0.00
1-Propanol	0.32	0.13	4.38	0.00
2-Butanol	0.01	0.02	0.42	0.00
1-Butanol	0.12	0.13	2.64	0.00
2-Pentanol	0.00	0.00	0.01	0.00
1-Pentanol	0.03	0.03	1.20	0.00
Water	55.56	105.92	30.53	0.00

Figure 4.11: Alcohol Distribution for Catalysts of Varying K Content

Detailed information on the individual compounds in the oil fraction of the liquid phase can be found in Appendix VIII. Table 4.20 shows the lumped distribution of the oil phase liquid products. These results are not consistent with those reported by Ma¹². Ma reported an oil fraction for all catalysts studied. Here, an oil fraction was not observed for the 0%K catalyst. Figure 4.12 contains data on the oil fraction selectivities by carbon number.

Table 4.20: Lumped Oil Product Distribution for Varied K Catalysts			
Catalysts	Selectivity		
	C ₆ -C ₈	C ₉ -C ₁₅	C ₁₆ +
0%K	0.0	0.0	0.0
0.45%K	40.7	59.3	0.0
0.9%K	48.8	51.2	0.0
1.8%K	34.1	58.2	7.8

Figure 4.12: Oil Fraction Selectivity for Varying K

Table 4.21 contains the liquid product properties. Two interesting things happen with these catalysts. The 0%K catalyst produces no detectable oil while the 1.8%K catalyst produces no detectable alcohol. The 1.8%K catalyst also has a very high olefin-to-paraffin ratio. Ma et al reported¹² that the olefin-to-paraffin ratio had a large increase with the addition of 0.9%K. Here, the large increase is not seen until the addition of 1.8%K.

Table 4.21: Liquid Product Properties for Catalysts of Varying K Composition						
Catalyst	Total Alcohol Weight (mg)	Percent Alcohol in Water	Total Oil Weight (mg)	Highest Carbon Number	$\frac{Alcohols}{HCs}$ (%)	$\frac{Olefins}{Paraffins}$ (%)
0%K	239	19.3	0	0	-	0.0
0.45%K	122	6.0	400	15	30.5	21.5
0.9%K	1460	72.6	675	20	216	15.1
1.8%K	0	0.0	2210	26	0.0	71.4

4.5 Data Analysis by Regression

In an attempt to understand better the large amount of data obtained over the course of this project, a regression model was employed for conversion, oil yield, olefin-to-paraffin ratio, gasoline yield and diesel yield. A regression model is defined²³ as “a mathematical expression that can quantitatively describe the variability among the observations, or responses, by partitioning an observation into two parts. The first part of the decomposition incorporates everything known about the magnitude of a response; the remaining portion is residual”.

The equation that was fit is as follows:

$$\begin{aligned}
 Y = & A_0 + A_1Fe + A_2Mo + A_3Cu + A_4K + A_5FeMo + \\
 & A_6FeCu + A_7FeK + A_8MoCu + A_9MoK + A_{10}CuK + \\
 & A_{11}FeMoCu + A_{12}FeMoK + A_{13}FeCuK + A_{14}MoCuK + \\
 & A_{15}FeMoCuK + A_{16}Fe^2 + A_{17}Mo^2 + A_{18}Cu^2 + A_{19}K^2
 \end{aligned}
 \tag{4.1}$$

The left side of the equation contains the dependent variable (i.e. conversion or oil yield). The right side of the equation contains the independent variables (i.e. the catalyst promoters) and the unknown coefficients.

To avoid statistical bias, the independent variables were normalized such that the base case values were set to 1. The equations used to normalize the variables are as follows:

$$Mo_N = \frac{Mo}{6} \quad (4.2)$$

$$Fe_N = \frac{Fe}{16} \quad (4.3)$$

$$Cu_N = \frac{Cu}{0.8} \quad (4.4)$$

$$K_N = \frac{K}{0.9} \quad (4.5)$$

The regression calculations were performed by a program called Minitab. This program performs a stepwise regression by backwards elimination. This process deletes terms deemed statistically insignificant as decided by the F-value. The F-value is a signal-to-noise ratio, and is defined:

$$F = \left(\frac{A_i}{S_{A_i}} \right)^2 \quad (4.6)$$

In other words, F is the square of the coefficient from the model (A_i) divided by the standard deviation of that term (S_{A_i}). The standard deviation is defined as:

$$S_{A_i} = \sqrt{\frac{\sum_n (y - y_p)^2}{(n - k - 1) \sum_n (x_i - x_{A_i})^2}} \quad (4.7)$$

where y is the observed value for the dependent variable

y_p is the predicted value for the dependent variable

n is the number of data points

k is the number of coefficients

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

x_{Ai} is the average value for the independent variable for the i-th parameter

The coefficient of determination (R^2) is an indication of how well the equation fits the data. R^2 is between 0 and 1 and is defined:

$$R^2 = \frac{\sum_n (y - y_A)^2 - \sum_n (y - y_p)^2}{\sum_n (y - y_A)^2} \quad (4.8)$$

where y_A is the average value for y

For CO conversion, the equation was determined to be:

$$\text{Conv} = 31.65 + 10.1\text{Fe}_N^2 - 15.7\text{Mo}_N \quad (4.9)$$

This gives the conversion in units of percent. This indicated that Fe and Mo are the most important terms, with increasing Mo decreasing conversion.

For oil fraction yield, the equation was determined to be:

$$\text{Oil} = 3268 - 4436 \text{Mo}_N + 920\text{Fe}_N\text{Mo}_N\text{K}_N + 1083\text{Mo}_N^2 \quad (4.10)$$

This gives the oil fraction yield in units of mg. This indicates that the most important terms are Mo and an interaction between Fe, Mo and K.

For the hydrocarbon production rate, the equation was determined to be:

$$\text{Hydro} = 126.68 + 304\text{Fe}_N - 163\text{Mo}_N \quad (4.11)$$

This gives the production rate of hydrocarbons in units of g/kg-cat/h. It depends positively on Fe and negatively on Mo.

For the Olefin-to-Paraffin ratio, the equation was determined to be:

$$\text{O/P} = 0.302 + 0.165\text{K}_N^2 - 0.276\text{Mo}_N \quad (4.12)$$

This gives the olefin-to-paraffin ratio as a unitless number. This indicates that K causes an increase in the olefin-to-paraffin ratio and Mo causes a decrease.

For the gasoline range production, the equation was determined to be:

$$\text{Gasoline} = 36.42 + 30\text{Fe}_N\text{K}_N \quad (4.13)$$

This gives the gasoline range production as a percentage. This indicates that an interaction between Fe and K is important to the production of gasoline range products.

For the diesel range production, the equation was determined to be:

$$\text{Diesel} = 65.58 + 29.5\text{Fe}_N\text{Cu}_N\text{K}_N - 31\text{Mo}_N\text{Cu}_N \quad (4.14)$$

This gives the diesel range production as a percentage. This indicates that an interaction between Fe, Cu and K is important to diesel range production along with an interaction between Mo and Cu.

Table 4.18 contains R^2 values for the previous equations.

Table 4.22: R^2 Values for the Regression Models	
Equation Number	R^2 Value
4.9 (Conversion)	0.65
4.10 (Oil production)	0.87
4.11 (Hydrocarbon production)	0.81
4.12 (O/P)	0.81
4.13 (Gasoline range)	0.37
4.14 (Diesel range)	0.58

This indicates that the equation for oil fraction yield and olefin-to-paraffin ratio is a good fit for the data. However, the gasoline range production has a very low R^2 value. So this relationship is less certain than the others. In any case, these equations can be used to formulate multi-component Fe-based catalysts appropriately, depending on what parameter is to be optimized.

4.6 Characterization of the Catalyst

Table 4.19 shows BET data for the base case catalyst before and after reaction. As expected, the values of the fresh catalyst decrease from the pre-impregnated support values in Table 3.1 and decrease still in the spent catalyst.

Table 4.23: BET Properties for Base Case Catalyst			
Catalyst	BET Surface Area (m ² /g)	Large-Pore Surface Area (m ² /g)	Macropore Volume > 2.0 nm (cm ³ /g)
Fresh	619.5	142.8	0.07
Spent	266.1	109.3	0.05

Figure 4.13 shows the XRD pattern for the base case catalyst before reaction. The two phases identifiable are the graphite from the support and magnetite, Fe₃O₄. The reason Cu and K are not visible in the XRD pattern is due to the low concentrations of both in the catalyst. Mo is not seen because Mo deposits as small particles and does not typically reduce until around 700°C as can be seen in the TPR data.

Figure 4.13: XRD Pattern for Base Case Catalyst Before Reaction

Figure 4.14 shows the XRD pattern of the base case catalyst after reaction has taken place. The two phases that can be identified are graphite from the support and Fe_2C . Iron carbides are considered the active phase for iron catalysts. It is possible that there was metallic iron present; however, the sample was exposed to air after reaction so any metallic iron would have been oxidized.

Figure 4.14: XRD Pattern for Base Case Catalyst After Reaction

Figure 4.15 shows TPR data for four different iron catalysts (0%, 8%, 16% and 32%). According to Ma et al²⁴, from 250-550°C, $\alpha\text{Fe}_2\text{O}_3$ is being reduced to Fe_3O_4 then Fe_3O_4 is being reduced to FeO . In the range of 400-700°C, there is a broad peak showing that FeO is being reduced to Fe metal. In the 0%Fe case, a negative peak is seen around 700°C, this is attributed to MoO_2 being reduced to MoC . The reason the peak is negative is due to a release of CO_2 during the reduction.

Figure 4.15: TPR Data for Varied Fe Catalysts

Table 4.24 contains the information on the H_2 uptake calculated from the TPR curves. This was done by integrating the area between 200-800°C as a single peak. From this, the degree of reduction was calculated. This was done by assuming that the Fe reduced by the following equation:

Then to discount the effect of the support and the other metals, the H_2 consumption of the 0%Fe catalyst was subtracted from the others. The degree of reduction is shown in Table 4.25. It is seen that the degree of reduction decreases as the metal concentration increases. This is likely due to less metal being exposed on the surface when present in higher concentrations.

Table 4.24: H ₂ Consumption for Varying Fe Catalysts	
Catalyst	H ₂ Consumption (μmol/g)
0%Fe	498
8%Fe	1068
16%Fe	1353
32%Fe	1427

Table 4.25: Degree of Reduction for Varying Fe Catalysts		
Catalyst	H ₂ Consumption (μmol/g)	Degree of Reduction (%)
0%Fe	0	0
8%Fe	570	27.1
16%Fe	855	19.7
32%Fe	929	10.9

4.7 Summary

The effects that four components, Mo, Fe, Cu and K, had on a catalyst were studied. The parameters looked at were the effects on gas-phase products, oil-phase products and aqueous-phase products. The data were compared to similar catalysts studied previously by Ma. In particular, the effects of K were compared to catalysts studied by Ma that contained only Fe and K. The effects of Cu were compared to catalysts studied by Ma that contained only Fe, Cu and K. The effects of Mo were compared to catalysts studied by Ma that contained Mo, Fe, Cu and K. The effect of Fe was never studied by Ma.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

The conclusions that can be drawn on the data obtained are as follows.

1. Adding Mo to the catalyst generally lowers the CO conversion, but causes an increase in stability. This is consistent with results reported by Ma using catalysts containing Mo, Fe, Cu and K. Adding Mo also lowers the production of CO₂ and increases CH₄ production. This is consistent with results reported by Ma. The addition of Mo increases aqueous production up to a loading of 6% and then the aqueous production decreases at 12% loading. This is consistent with results reported by Ma. An increase in Mo loading causes a decrease in total oil production as well as the olefin-to-paraffin ratio. This is inconsistent with Ma. He reported similar ratios across catalysts containing 0-12% Mo.
2. Adding Fe to the catalysts causes an increase in CO conversion. Adding Fe also causes an increase in CO₂ production and a decrease in CH₄ production. Changing the Fe loading of the catalyst had a small effect on aqueous production while the oil production increased with increasing Fe loading.
3. Changes in Cu loading had very small effects on all parameters. This is consistent with data reported by Ma using simpler catalysts, catalysts containing only Fe, Cu and K.
4. The absence of K causes a very low CO conversion while all other K loadings studied have comparable CO conversions. This is consistent with reports by Ma

using simpler catalysts, catalysts containing only Fe and K. Increases in K loading causes an increase in CO₂ production and a decrease in CH₄ production. This is consistent with reports by Ma using simpler catalyst. Increases in K loading caused an increase in oil production.

5. The regression equations for the olefin-to-paraffin ratio and the oil fraction yield gave a well-fitted equation while the gasoline production gave an equation that did not fit very well.

5.2 Recommendations for Future Work

Based on the data, these are recommendations for future work in the area.

1. The effect of varying multiple promoters at once should be investigated.
2. The effect of varying reaction conditions (i.e. temperature, flowrate and pressure) should be investigated.
3. Stability studies should be performed as well.

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Appendix I

Data for Aqueous Phase

for

Varied Mo Catalysts

0%Mo, 16% Fe, 0.8% Cu, 0.9% K

Total Volume (mL)	0.7	Sample Volume (mL)	0.60	Total Weight (mg)	674.5
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	684039	6837661.4	2822397	32200	31127.5
Ethanol	4022392	41860601.6	2822397	32200	113995.8
2-Propanol	60120	34298463.6	2822397	32200	2233.1
1-Propanol	1194446	11557899.8	2822397	32200	44660.1
2-Butanol	0	0.0	2822397	32200	0.0
1-Butanol	588255	6801721.8	2822397	32200	32276.1
2-Pentanol	0	0.0	2822397	32200	0.0
1-Pentanol	247949	2992494.7	2822397	32200	14922.3
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	36.315	1.133		
Ethanol	46.07	132.995	2.887		
2-Propanol	60.10	2.605	0.043		
1-Propanol	60.10	52.103	0.867		
2-Butanol	74.13	0.000	0.000	Total Oxygenate	
1-Butanol	74.13	37.655	0.508	Weight (mg) (based on	239.21
2-Pentanol	88.16	0.000	0.000	sample volume)	
1-Pentanol	88.16	17.409	0.197	Total Oxygenate	
Water	18.01	395.416	21.955	Weight (mg) (based on	279.08
				total volume)	
				Weight Percent of	58.62
				Water	

3% Mo, 16% Fe, 0.8% Cu, 0.9% K

Total Volume (mL)	1.1	Sample Volume (mL)	1.00	Total Weight (mg)	1092
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	1695497	17745284.5	2486334	29700	80782.9
Ethanol	6730233	73334845.9	2486334	29700	199707.2
2-Propanol	850400	507970107.1	2486334	29700	33073.3
1-Propanol	1780927	18043373.3	2486334	29700	69720.1
2-Butanol	653890	418561813.3	2486334	29700	10419.8
1-Butanol	1872088	22664112.0	2486334	29700	107547.5
2-Pentanol	334900	25885393.0	2486334	29700	489.0
1-Pentanol	1114289	14080824.5	2486334	29700	70215.2
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	88.861	2.773		
Ethanol	46.07	219.678	4.768		
2-Propanol	60.10	36.381	0.605		
1-Propanol	60.10	76.692	1.276	Total Oxygenate	
2-Butanol	74.13	11.462	0.155	Weight (mg) (based on	571.95
1-Butanol	74.13	118.302	1.596	sample volume)	
2-Pentanol	88.16	0.538	0.006	Total Oxygenate	
1-Pentanol	88.16	77.237	0.876	Weight (mg) (based on	629.15
Water	18.01	462.850	25.700	total volume)	
				Weight Percent of	42.39
				Water	

6%Mo, 16%Fe, 0.8%Cu, 0.9%K

Total Volume (mL)	2.2	Sample Volume (mL)	0.80	Total Weight (mg)	2010
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)
Methanol	84286	19451	22.2	383.7
Ethanol	82843	16693	18.3	225.6
2-Propanol	12534417	290032	5.8	816.1
1-Propanol	78959	16539	19.5	305.1
2-Butanol	31995228	1832669	34.2	796.5
1-Butanol	82482	18344	18.1	391.4
2-Pentanol	41499452	135882	21	783.9
1-Pentanol	77869	19888	18.8	388.3

X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	2866151	20982610.3	4260676	35600	95520.3
Ethanol	9081517	69217066.9	4260676	35600	188493.5
2-Propanol	1111808	464535818.8	4260676	35600	30245.3
1-Propanol	3493646	24758539.4	4260676	35600	95667.8
2-Butanol	1002701	448952985.4	4260676	35600	11176.4
1-Butanol	1769821	14987054.9	4260676	35600	71117.7
2-Pentanol	392102	21198892.9	4260676	35600	400.4
1-Pentanol	869456	7685150.2	4260676	35600	38322.6

	MW	Weight (mg)	mmol_{sample}
Methanol	32.04	262.681	8.199
Ethanol	46.07	518.357	11.252
2-Propanol	60.10	83.175	1.384
1-Propanol	60.10	263.086	4.377
2-Butanol	74.13	30.735	0.415
1-Butanol	74.13	195.574	2.638
2-Pentanol	88.16	1.101	0.012
1-Pentanol	88.16	105.387	1.195
Water	18.01	549.904	30.533

Total Oxygenate	
Weight (mg) (based on sample volume)	530.94
Total Oxygenate	
Weight (mg) (based on total volume)	1460.10
Weight Percent of Water	27.36

12% Mo, 16% Fe, 0.8% Cu, 0.9% K

Total Volume (mL)	1	Sample Volume (mL)	0.90	Total Weight (mg)	923.9
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	3009121	29917491.7	2220772	25200	136195.1
Ethanol	5954056	61630087.8	2220772	25200	167832.5
2-Propanol	607818	344895913.5	2220772	25200	22455.7
1-Propanol	1614686	15540295.9	2220772	25200	60048.2
2-Butanol	444402	270228095.3	2220772	25200	6727.1
1-Butanol	1015399	11677470.2	2220772	25200	55412.8
2-Pentanol	132728	9745446.8	2220772	25200	184.1
1-Pentanol	525481	6307929.7	2220772	25200	31455.0
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	151.328	4.723		
Ethanol	46.07	186.481	4.048		
2-Propanol	60.10	24.951	0.415	Total Oxygenate	
1-Propanol	60.10	66.720	1.110	Weight (mg) (based on	480.31
2-Butanol	74.13	7.475	0.101	sample volume)	
1-Butanol	74.13	61.570	0.831	Total Oxygenate	
2-Pentanol	88.16	0.205	0.002	Weight (mg) (based on	533.68
1-Pentanol	88.16	34.950	0.396	total volume)	
Water	18.01	390.222	21.667	Weight Percent of	42.24
				Water	

Appendix II

Data for Oil Phase

for

Varied Mo Catalysts

0%Mo, 16% Fe, 0.8% Cu, 0.9% K

Injection Volume (µL)	0.1	Total Volume (µL)	4300	Total Weight (mg)	3660
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Correction factor	0.845706583
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Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	3.6859	74517	4.284	184.232	155.806	1.807	4.283
C ₇ (parafin)	100.23	11.5904	234635	14.531	624.848	528.438	5.272	14.528
C ₇ (olefin)	98.21	5.2102	105475	6.266	269.423	227.853	2.320	6.264
C ₈ (parafin)	114.26	11.6439	235717	14.601	627.826	530.956	4.647	14.597
C ₈ (olefin)	112.24	6.8804	139286	8.429	362.465	306.539	2.731	8.427
C ₉ (i-parafin)	128.29	2.9368	59452	3.320	142.776	120.746	0.941	3.320
C ₉ (parafin)	128.29	5.8881	119198	7.144	307.186	259.789	2.025	7.142
C ₉ (olefin)	126.27	6.3436	128418	7.734	332.558	281.246	2.227	7.732
C ₁₀ (parafin)	142.32	5.9412	120272	7.213	310.142	262.289	1.843	7.211
C ₁₀ (olefin)	140.30	4.8113	97398	5.749	247.196	209.056	1.490	5.747
C ₁₁ (parafin)	156.35	3.7274	75458	4.345	186.821	157.996	1.011	4.344
C ₁₁ (olefin)	154.33	3.046	61663	3.462	148.860	125.892	0.816	3.461
C ₁₂ (parafin)	170.38	3.003	60792	3.406	146.463	123.865	0.727	3.405
C ₁₂ (olefin)	168.36	2.1099	42713	2.249	96.713	81.791	0.486	2.249
C ₁₃ (parafin)	184.41	2.0602	41706	2.185	93.942	79.447	0.431	2.184
C ₁₃ (olefin)	182.39	1.5695	31773	1.549	66.608	56.331	0.309	1.549
C ₁₄ (parafin)	198.44	1.3516	27361	1.267	54.467	46.063	0.232	1.266
C ₁₄ (olefin)	196.42	1.2472	25249	1.132	48.655	41.148	0.209	1.131
C ₁₅ (parafin)	212.47	0.871	17632	0.644	27.694	23.421	0.110	0.644
C ₁₆ ⁺	226.50	0.53	15616	0.515	22.147	18.730	0.083	0.515

Total	100.024	4301.021	3637.402	29.718	100.000
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3%Mo, 16% Fe, 0.8% Cu, 0.9% K

Injection Volume (µL)	0.1	Total Volume (µL)	900	Total Weight (mg)	737.4
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Correction factor	1.06564517
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Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	1.2478	20894	0.853	7.675	8.179	0.0949	1.106
C ₇ (parafin)	100.23	9.5072	159193	9.703	87.330	93.063	0.9285	12.581
C ₇ (olefin)	98.21	1.3257	22198	0.936	8.426	8.979	0.0914	1.214
C ₈ (i-parafin)	114.26	1.3375	22396	0.949	8.540	9.101	0.0797	1.230
C ₈ (parafin)	114.26	13.4508	225227	13.929	125.364	133.593	1.1692	18.060
C ₈ (olefin)	112.24	3.7764	63234	3.562	32.062	34.166	0.3044	4.619
C ₉ (i-parafin)	128.29	1.9614	32843	1.617	14.557	15.513	0.1209	2.097
C ₉ (parafin)	128.29	12.7134	212880	13.139	118.252	126.015	0.9823	17.036
C ₉ (olefin)	126.27	2.5448	42612	2.243	20.184	21.509	0.1703	2.908
C ₁₀ (parafin)	142.32	9.3215	156084	9.504	85.540	91.155	0.6405	12.323
C ₁₀ (olefin)	140.30	3.4384	57575	3.200	28.802	30.693	0.2188	4.149
C ₁₁ (parafin)	156.35	5.9665	99907	5.909	53.184	56.675	0.3625	7.662
C ₁₁ (olefin)	154.33	2.0167	33769	1.677	15.091	16.081	0.1042	2.174
C ₁₂ (parafin)	170.38	4.1101	68822	3.920	35.280	37.596	0.2207	5.082
C ₁₂ (olefin)	168.36	1.2152	20348	0.818	7.361	7.844	0.0466	1.060
C ₁₃ (parafin)	184.41	2.6822	44912	2.390	21.509	22.921	0.1243	3.099
C ₁₃ (olefin)	182.39	0.5761	9646	0.133	1.197	1.275	0.0070	0.172
C ₁₄ (parafin)	198.44	1.6031	26842	1.233	11.101	11.830	0.0596	1.599
C ₁₅ ⁺	212.47	1.768	29606	1.410	12.693	13.526	0.0637	1.829
Total				77.128	694.148	739.716	5.789	100.000

6%Mo, 16% Fe, 0.8% Cu, 0.9% K

Injection Volume (µL)	0.1	Total Volume (µL)	1000	Total Weight (mg)	674.5
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Correction factor	0.647836391
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Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	5.5722	109924	6.550	65.504	42.436	0.492	6.414
C ₇ (parafin)	100.23	13.8787	273786	17.037	170.369	110.371	1.101	16.683
C ₇ (olefin)	98.21	3.033	59832	3.345	33.447	21.668	0.221	3.275
C ₈ (i-parafin)	114.26	1.6592	32731	1.610	16.103	10.432	0.091	1.577
C ₈ (parafin)	114.26	15.3226	302271	18.860	188.598	122.181	1.069	18.468
C ₈ (olefin)	112.24	2.2888	45152	2.405	24.052	15.582	0.139	2.355
C ₉ (i-parafin)	128.29	1.944	38349	1.970	19.699	12.761	0.099	1.929
C ₉ (parafin)	128.29	12.0555	237820	14.735	147.352	95.460	0.744	14.429
C ₉ (olefin)	126.27	1.4649	28899	1.365	13.651	8.844	0.070	1.337
C ₁₀ (parafin)	142.32	8.0837	159469	9.721	97.210	62.976	0.442	9.519
C ₁₀ (olefin)	140.30	2.5608	50516	2.748	27.485	17.806	0.127	2.691
C ₁₁ (parafin)	156.35	5.0808	100229	5.930	59.299	38.416	0.246	5.807
C ₁₁ (olefin)	154.33	1.5156	29899	1.429	14.291	9.258	0.060	1.399
C ₁₂ (parafin)	170.38	3.2896	64894	3.669	36.686	23.767	0.139	3.592
C ₁₂ (olefin)	168.36	0.8171	16120	0.547	5.473	3.546	0.021	0.536
C ₁₃ (parafin)	184.41	2.3217	45800	2.447	24.467	15.851	0.086	2.396
C ₁₃ (olefin)	182.39	0.4737	9344	0.114	1.137	0.736	0.004	0.111
C ₁₄ ⁺	198.44	6.3565	126940	7.639	76.393	49.490	0.249	7.481

Total	102.122	1021.215	661.580	5.402	100.000
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Appendix III

Data for Aqueous Phase

for

Varied Fe Catalysts

6% Mo, 8% Fe, 0.8% Cu, 0.9% K

Total Volume (mL)	1.8	Sample Volume (mL)	0.60	Total Weight (mg)	1690
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	1074417	17087963.1	1052216	19100	77790.5
Ethanol	3374332	55872689.9	1052216	19100	152153.8
2-Propanol	333098	302355877.2	1052216	19100	19686.0
1-Propanol	1411139	21725655.9	1052216	19100	83948.6
2-Butanol	266476	259205668.1	1052216	19100	6452.8
1-Butanol	499412	9187617.5	1052216	19100	43597.8
2-Pentanol	72455	8510194.0	1052216	19100	160.8
1-Pentanol	221958	4262187.3	1052216	19100	21253.7
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	233.372	7.284		
Ethanol	46.07	456.461	9.908		
2-Propanol	60.10	59.058	0.983		
1-Propanol	60.10	251.846	4.190	Total Oxygenate	
2-Butanol	74.13	19.358	0.261	Weight (mg) (based on	405.04
1-Butanol	74.13	130.793	1.764	sample volume)	
2-Pentanol	88.16	0.482	0.005	Total Oxygenate	
1-Pentanol	88.16	63.761	0.723	Weight (mg) (based on	1215.13
Water	18.01	474.868	26.367	total volume)	
				Weight Percent of	28.10
				Water	

6% Mo, 32% Fe, 0.8% Cu, 0.9% K

Total Volume (mL)	2.45	Sample Volume (mL)	1.00	Total Weight (mg)	2230
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	1810043	21808990.2	2588763	35600	99282.3
Ethanol	6081735	76290155.7	2588763	35600	207755.1
2-Propanol	836403	575163358.4	2588763	35600	37448.2
1-Propanol	219443	2559493.7	2588763	35600	9890.0
2-Butanol	657169	484275726.7	2588763	35600	12055.7
1-Butanol	1047284	14596127.2	2588763	35600	69262.7
2-Pentanol	249181	22172530.7	2588763	35600	418.8
1-Pentanol	779228	11335887.2	2588763	35600	56527.3
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	243.242	7.592		
Ethanol	46.07	509.000	11.048		
2-Propanol	60.10	91.748	1.527		
1-Propanol	60.10	24.230	0.403		
2-Butanol	74.13	29.537	0.398		
1-Butanol	74.13	169.694	2.289		
2-Pentanol	88.16	1.026	0.012		
1-Pentanol	88.16	138.492	1.571		
Water	18.01	1023.032	56.804		
				Total Oxygenate	
				Weight (mg) (based on	492.64
				sample volume)	
				Total Oxygenate	
				Weight (mg) (based on	1206.97
				total volume)	
				Weight Percent of	45.88
				Water	

Appendix IV

Data for Oil Phase

for

Varied Fe Catalysts

6%Mo, 8%Fe, 0.8%Cu, 0.9%K

Injection Volume (µL)	0.1	Total Volume (µL)	800	Total Weight (mg)	550
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Correction factor	0.545618441
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Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	2.9188	66404	3.765	30.122	16.435	0.191	3.128
C ₇ (parafin)	100.23	10.0247	228066	14.111	112.888	61.594	0.615	11.721
C ₇ (olefin)	98.21	2.326	52918	2.902	23.218	12.668	0.129	2.411
C ₈ (i-parafin)	114.26	4.1712	94897	5.589	44.710	24.394	0.213	4.642
C ₈ (parafin)	114.26	10.5489	239992	14.874	118.993	64.925	0.568	12.355
C ₈ (olefin)	112.24	2.6916	61236	3.435	27.476	14.992	0.134	2.853
C ₉ (i-parafin)	128.29	2.6273	59772	3.341	26.727	14.583	0.114	2.775
C ₉ (parafin)	128.29	11.4025	259411	16.117	128.935	70.350	0.548	13.388
C ₉ (olefin)	126.27	1.182	26890	1.237	9.892	5.397	0.043	1.027
C ₁₀ (parafin)	142.32	8.8726	201854	12.434	99.468	54.272	0.381	10.328
C ₁₀ (olefin)	140.30	3.3261	74190	4.264	34.108	18.610	0.133	3.542
C ₁₁ (parafin)	156.35	6.7715	154054	9.375	74.996	40.919	0.262	7.787
C ₁₁ (olefin)	154.33	2.7561	62702	3.528	28.227	15.401	0.100	2.931
C ₁₂ (parafin)	170.38	4.9647	112949	6.744	53.952	29.437	0.173	5.602
C ₁₂ (olefin)	168.36	1.8274	41574	2.176	17.410	9.499	0.056	1.808
C ₁₃ (parafin)	184.41	4.3845	99750	5.899	47.194	25.750	0.140	4.900
C ₁₃ (olefin)	182.39	1.4406	32773	1.613	12.904	7.041	0.039	1.340
C ₁₄ (parafin)	198.44	2.9533	67188	3.815	30.523	16.654	0.084	3.169
C ₁₄ (olefin)	196.42	1.8224	41464	2.169	17.354	9.468	0.048	1.802
C ₁₅ (parafin)	212.47	1.7134	38980	2.010	16.082	8.775	0.041	1.670

C ₁₆ (parafin)	226.50	1.0127	23040	0.990	7.921	4.322	0.019	0.822
C ₁₇ (parafin)	240.53	2.2792	51853	2.834	22.672	12.371	0.051	2.354
C ₁₇ (olefin)	238.51	0.4089	9303	0.111	0.888	0.485	0.002	0.092
Total				120.388	963.100	525.485	4.030	100.000

6%Mo, 32%Fe, 0.8%Cu, 0.9%K

Injection Volume (µL)	0.1	Total Volume (µL)	2550	Total Weight (mg)	1570
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Correction factor	0.393434017
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Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	3.2114	90542	5.310	135.405	53.273	0.618	3.600
C ₇ (parafin)	100.23	16.1701	455894	28.691	731.621	287.845	2.872	19.450
C ₈ (i-parafin)	114.26	2.0792	58619	3.267	83.310	32.777	0.287	2.215
C ₈ (parafin)	114.26	15.8388	446551	28.093	716.374	281.846	2.467	19.045
C ₈ (olefin)	112.24	2.29	64562	3.647	93.008	36.593	0.326	2.473
C ₉ (parafin)	128.29	11.9455	336785	21.069	537.248	211.372	1.648	14.283
C ₉ (olefin)	126.27	3.8185	107658	6.405	163.336	64.262	0.509	4.342
C ₁₀ (parafin)	142.32	8.3771	236181	14.630	373.073	146.779	1.031	9.918
C ₁₀ (olefin)	140.30	3.0461	85880	5.012	127.797	50.280	0.358	3.398
C ₁₁ (parafin)	156.35	5.3524	150902	9.173	233.906	92.027	0.589	6.218
C ₁₁ (olefin)	154.33	1.8583	52393	2.869	73.150	28.780	0.186	1.945
C ₁₂ (parafin)	170.38	3.4974	98604	5.826	148.561	58.449	0.343	3.950
C ₁₂ (olefin)	168.36	1.441	40626	2.116	53.947	21.225	0.126	1.434
C ₁₃ (parafin)	184.41	2.3312	65725	3.722	94.906	37.339	0.202	2.523
C ₁₃ (olefin)	182.39	1.0322	29102	1.378	35.141	13.826	0.076	0.934
C ₁₄ (parafin)	198.44	1.4788	41694	2.184	55.690	21.910	0.110	1.481
C ₁₄ (olefin)	196.42	0.6216	17526	0.637	16.250	6.393	0.033	0.432
C ₁₅ (parafin)	212.47	0.8708	24647	1.093	27.871	10.965	0.052	0.741
C ₁₅ (olefin)	210.45	0.3466	9771	0.141	3.595	1.414	0.007	0.096
C ₁₆ ⁺	226.50	1.5132	42664	2.246	57.273	22.533	0.099	1.523

Total	147.508	3761.464	1479.888	11.939	100.000
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Appendix V

Data for Aqueous Phase

for

Varied Cu Catalysts

6% Mo, 16% Fe, 0%Cu, 0.9% K

Total Volume (mL)	1.5	Sample Volume (mL)	0.80	Total Weight (mg)	1450
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	2629424	18384837.7	4072613	32500	83694.4
Ethanol	7960369	57946434.8	4072613	32500	157801.1
2-Propanol	1325732	529034361.3	4072613	32500	34444.8
1-Propanol	3002166	20319805.9	4072613	32500	78516.4
2-Butanol	894953	382708734.0	4072613	32500	9527.3
1-Butanol	1975408	15976531.2	4072613	32500	75813.1
2-Pentanol		0.0	4072613	32500	0.0
1-Pentanol	4648867	39245566.4	4072613	32500	195701.2
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	156.927	4.898		
Ethanol	46.07	295.877	6.422		
2-Propanol	60.10	64.584	1.075		
1-Propanol	60.10	147.218	2.450	Total Oxygenate	
2-Butanol	74.13	17.864	0.241	Weight (mg) (based on	635.50
1-Butanol	74.13	142.150	1.918	sample volume)	
2-Pentanol	88.16	0.000	0.000	Total Oxygenate	
1-Pentanol	88.16	366.940	4.162	Weight (mg) (based on	1191.56
Water	18.01	258.441	14.350	total volume)	
				Weight Percent of	17.82
				Water	

6% Mo, 16% Fe, 0.4% Cu, 0.9% K

Total Volume (mL)	1.5	Sample Volume (mL)	1.00	Total Weight (mg)	1350
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	2651079	32725601.0	1447952	20400	148978.6
Ethanol	7260776	93313041.4	1447952	20400	254112.3
2-Propanol	950885	669918425.3	1447952	20400	43617.5
1-Propanol	1814886	21687025.4	1447952	20400	83799.3
2-Butanol	536600	405120852.9	1447952	20400	10085.2
1-Butanol	1123443	16041409.0	1447952	20400	76120.9
2-Pentanol	124762	11373679.0	1447952	20400	214.8
1-Pentanol	403851	6019084.3	1447952	20400	30014.6
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	223.468	6.975		
Ethanol	46.07	381.168	8.274		
2-Propanol	60.10	65.426	1.089		
1-Propanol	60.10	125.699	2.091	Total Oxygenate	
2-Butanol	74.13	15.128	0.204	Weight (mg) (based on	646.94
1-Butanol	74.13	114.181	1.540	sample volume)	
2-Pentanol	88.16	0.322	0.004	Total Oxygenate	
1-Pentanol	88.16	45.022	0.511	Weight (mg) (based on	970.42
Water	18.01	379.585	21.076	total volume)	
				Weight Percent of	28.12
				Water	

6% Mo, 16% Fe, 1.6% Cu, 0.9% K

Total Volume (mL)	0.8	Sample Volume (mL)	0.70	Total Weight (mg)	717.2
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	2405140	21332994.4	2765894	28000	97115.4
Ethanol	6743497	62271735.8	2765894	28000	169579.9
2-Propanol	948178	479987908.8	2765894	28000	31251.4
1-Propanol	1818540	15614209.2	2765894	28000	60333.8
2-Butanol	697644	378455037.4	2765894	28000	9421.4
1-Butanol	1402161	14385860.7	2765894	28000	68264.9
2-Pentanol	256919	16829118.1	2765894	28000	317.9
1-Pentanol	791512	8476435.6	2765894	28000	42268.4
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	110.989	3.464		
Ethanol	46.07	193.806	4.207		
2-Propanol	60.10	35.716	0.594		
1-Propanol	60.10	68.953	1.147		
2-Butanol	74.13	10.767	0.145		
1-Butanol	74.13	78.017	1.052		
2-Pentanol	88.16	0.363	0.004		
1-Pentanol	88.16	48.307	0.548		
Water	18.01	170.282	9.455		
				Total Oxygenate	
				Weight (mg) (based on	478.55
				sample volume)	
				Total Oxygenate	
				Weight (mg) (based on	546.92
				total volume)	
				Weight Percent of	23.74
				Water	

Appendix VI

Data for Oil Phase

for

Varied Cu Catalysts

6%Mo, 16%Fe, 0%Cu, 0.9%K

Injection Volume (µL)	0.1	Total Volume (µL)	1000	Total Weight (mg)	900
Correction factor	0.807249237				

Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	3.3005	80436	4.663	46.633	37.644	0.437	4.227
C ₇ (parafin)	100.23	10.8628	264734	16.458	164.576	132.854	1.325	14.918
C ₇ (olefin)	98.21	1.4171	34535	1.726	17.258	13.931	0.142	1.564
C ₈ (i-parafin)	114.26	1.8641	45429	2.423	24.229	19.559	0.171	2.196
C ₈ (parafin)	114.26	12.6777	308965	19.288	192.882	155.704	1.363	17.484
C ₈ (olefin)	112.24	1.3204	32179	1.575	15.750	12.714	0.113	1.428
C ₉ (i-parafin)	128.29	1.1822	28812	1.360	13.595	10.975	0.086	1.232
C ₉ (parafin)	128.29	10.2082	248782	15.437	154.367	124.613	0.971	13.993
C ₉ (olefin)	126.27	1.5706	38277	1.965	19.653	15.864	0.126	1.781
C ₁₀ (parafin)	142.32	7.1482	174207	10.664	106.642	86.087	0.605	9.667
C ₁₀ (olefin)	140.30	2.2265	54261	2.988	29.882	24.122	0.172	2.709
C ₁₁ (parafin)	156.35	4.987	121535	7.293	72.934	58.876	0.377	6.611
C ₁₁ (olefin)	154.33	1.7479	42598	2.242	22.418	18.097	0.117	2.032
C ₁₂ (parafin)	170.38	3.4596	84312	4.911	49.113	39.646	0.233	4.452
C ₁₂ (olefin)	168.36	1.1235	27382	1.268	12.680	10.236	0.061	1.149
C ₁₃ (parafin)	184.41	2.6928	65626	3.715	37.155	29.993	0.163	3.368
C ₁₃ (olefin)	182.39	0.8751	21326	0.880	8.805	7.107	0.039	0.798
C ₁₄ (parafin)	198.44	2.3507	57289	3.182	31.819	25.686	0.129	2.884
C ₁₄ (olefin)	196.42	0.9203	22428	0.951	9.510	7.677	0.039	0.862
C ₁₅ (parafin)	212.47	2.7779	67699	3.848	38.481	31.064	0.146	3.488
C ₁₅ (olefin)	210.45	1.3047	31796	1.550	15.505	12.516	0.059	1.405

C ₁₆ (parafin)	226.50	1.547	37702	1.928	19.285	15.567	0.069	1.748
C ₁₆ (olefin)	224.48	1.4575	35521	1.789	17.889	14.441	0.064	1.622
C ₁₇ ⁺	240.53	0.7853	19139	0.740	7.405	5.978	0.025	0.671
Total				110.317	1103.170	890.533	6.942	100.000

6%Mo, 16%Fe, 0.4%Cu, 0.9%K

Injection Volume (µL)		0.1	Total Volume (µL)		1000	Total Weight (mg)		950
Correction factor		0.326860828						
Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	3.5371	161179	9.830	98.305	32.132	0.373	3.748
C ₇ (i-parafin)	99.23	0.8682	39564	2.048	20.476	6.693	0.067	0.781
C ₇ (parafin)	100.23	11.5858	527942	33.302	333.018	108.851	1.086	12.696
C ₇ (olefin)	98.21	0.7068	32205	1.577	15.767	5.154	0.052	0.601
C ₈ (i-parafin)	113.26	2.0804	94798	5.582	55.824	18.247	0.161	2.128
C ₈ (parafin)	114.26	15.4151	702434	44.469	444.686	145.350	1.272	16.953
C ₈ (olefin)	112.24	1.8852	85903	5.013	50.131	16.386	0.146	1.911
C ₉ (i-parafin)	128.29	1.3373	60938	3.415	34.155	11.164	0.087	1.302
C ₉ (parafin)	128.29	13.1524	599325	37.870	378.700	123.782	0.965	14.438
C ₉ (olefin)	126.27	2.3088	105209	6.249	62.486	20.424	0.162	2.382
C ₁₀ (parafin)	142.32	9.9107	451608	28.417	284.167	92.883	0.653	10.834
C ₁₀ (olefin)	140.30	3.054	139163	8.422	84.215	27.527	0.196	3.211
C ₁₁ (parafin)	156.35	6.9129	315008	19.675	196.749	64.310	0.411	7.501
C ₁₁ (olefin)	154.33	2.1269	96919	5.718	57.181	18.690	0.121	2.180
C ₁₂ (parafin)	170.38	4.8858	222639	13.764	137.637	44.988	0.264	5.247
C ₁₂ (olefin)	168.36	1.6164	73658	4.229	42.295	13.825	0.082	1.612
C ₁₃ (parafin)	184.41	3.6225	165068	10.079	100.794	32.945	0.179	3.843
C ₁₃ (olefin)	182.39	1.2083	55061	3.039	30.394	9.934	0.054	1.159
C ₁₄ (parafin)	198.44	2.7544	125514	7.548	75.481	24.672	0.124	2.878
C ₁₄ (olefin)	196.42	0.9018	41096	2.146	21.457	7.013	0.036	0.818

C ₁₅ (parafin)	212.47	1.9221	87587	5.121	51.209	16.738	0.079	1.952
C ₁₅ (olefin)	210.45	0.6681	30446	1.464	14.641	4.786	0.023	0.558
C ₁₆ (parafin)	226.50	1.3053	59478	3.322	33.220	10.858	0.048	1.267
C ₁₆ (olefin)	224.48	0.5189	23646	1.029	10.289	3.363	0.015	0.392
C ₁₇ ⁺	240.53	1.8009	82065	4.768	47.675	15.583	0.065	1.818

Total	262.299	2622.986	857.351	6.642	100.000
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6%Mo, 16%Fe, 1.6%Cu, 0.9%K

Injection Volume (µL)	0.1	Total Volume (µL)	1200	Total Weight (mg)	970
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Correction factor	0.321119469
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Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	7.5541	307955	19.224	230.682	74.077	0.859	8.339
C ₇ (i-parafin)	100.23	1.9492	79463	4.601	55.212	17.730	0.177	1.996
C ₇ (parafin)	100.23	13.7958	562404	35.507	426.087	136.825	1.365	15.402
C ₇ (olefin)	98.21	1.2727	51885	2.836	34.033	10.929	0.111	1.230
C ₈ (i-parafin)	114.26	2.2517	91796	5.390	64.683	20.771	0.182	2.338
C ₈ (parafin)	114.26	14.6101	595605	37.632	451.584	145.012	1.269	16.324
C ₈ (olefin)	112.24	1.7458	71169	4.070	48.842	15.684	0.140	1.766
C ₉ (i-parafin)	128.29	1.332	54300	2.991	35.888	11.524	0.090	1.297
C ₉ (parafin)	128.29	11.9283	486272	30.635	367.621	118.050	0.920	13.289
C ₉ (olefin)	126.27	2.0842	84963	4.953	59.436	19.086	0.151	2.148
C ₁₀ (parafin)	142.32	8.4194	343228	21.481	257.770	82.775	0.582	9.318
C ₁₀ (olefin)	140.30	2.6297	107203	6.376	76.515	24.570	0.175	2.766
C ₁₁ (parafin)	156.35	5.8297	237657	14.725	176.697	56.741	0.363	6.387
C ₁₁ (olefin)	154.33	1.9283	78609	4.546	54.556	17.519	0.114	1.972
C ₁₂ (parafin)	170.38	4.0273	164179	10.022	120.270	38.621	0.227	4.347
C ₁₂ (olefin)	168.36	1.2054	49138	2.660	31.924	10.251	0.061	1.154
C ₁₃ (parafin)	184.41	2.7937	113889	6.804	81.649	26.219	0.142	2.951
C ₁₃ (olefin)	182.39	0.7859	32040	1.566	18.793	6.035	0.033	0.679
C ₁₄ (parafin)	198.44	1.8887	76996	4.443	53.317	17.121	0.086	1.927
C ₁₄ (olefin)	196.42	0.4707	19191	0.744	8.926	2.866	0.015	0.323

C ₁₅ (parafin)	212.47	1.3661	55690	3.080	36.955	11.867	0.056	1.336
C ₁₅ (olefin)	210.45	0.313	12764	0.333	3.990	1.281	0.006	0.144
C ₁₆ ⁺	226.50	2.4532	100008	5.916	70.989	22.796	0.101	2.566
Total	230.535	2766.420	888.351	7.224	100.000			

Appendix VII

Data for Aqueous Phase

for

Varied K Catalysts

6%Mo, 16% Fe, 0.9% Cu, 0% K

Total Volume (mL)	1.5	Sample Volume (mL)	0.80	Total Weight (mg)	1240
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	1543133	14599075.6	1435485	15500	66460.2
Ethanol	1600581	15765000.9	1435485	15500	42931.6
2-Propanol	45167	24387776.6	1435485	15500	1587.9
1-Propanol	290260	2658244.1	1435485	15500	10271.5
2-Butanol	33615	19450200.5	1435485	15500	484.2
1-Butanol	89761	982282.0	1435485	15500	4661.2
2-Pentanol		0.0	1435485	15500	0.0
1-Pentanol	23104	263908.6	1435485	15500	1316.0
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	124.613	3.889		
Ethanol	46.07	80.497	1.747		
2-Propanol	60.10	2.977	0.050	Total Oxygenate	
1-Propanol	60.10	19.259	0.320	Weight (mg) (based on	127.71
2-Butanol	74.13	0.908	0.012	sample volume)	
1-Butanol	74.13	8.740	0.118	Total Oxygenate	
2-Pentanol	88.16	0.000	0.000	Weight (mg) (based on	239.46
1-Pentanol	88.16	2.468	0.028	total volume)	
Water	18.01	1000.539	55.555	Weight Percent of	80.69
				Water	

6% Mo, 16% Fe, 0.8% Cu, 0.45% K

Total Volume (mL)	2.35	Sample Volume (mL)	0.80	Total Weight (mg)	2030
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X_{standard}	A_{x, standard}	A_{cyclohexanol, standard}	Wt_{cyclohexanol, standard}(μg)	Wt_{x, standard}(μg)	
Methanol	84286	19451	22.2	383.7	
Ethanol	82843	16693	18.3	225.6	
2-Propanol	12534417	290032	5.8	816.1	
1-Propanol	78959	16539	19.5	305.1	
2-Butanol	31995228	1832669	34.2	796.5	
1-Butanol	82482	18344	18.1	391.4	
2-Pentanol	41499452	135882	21	783.9	
1-Pentanol	77869	19888	18.8	388.3	
X_{sample}	A_{x, sample}	A_{corrected,x, sample}	A_{cyclohexanol, sample}	Wt_{cyclohexanol, sample}(μg)	Wt_{x, sample}(μg)
Methanol	2661786	3404105.9	15688973	22900	15496.7
Ethanol	4733160	6301957.3	15688973	22900	17161.6
2-Propanol	371253	27097477.4	15688973	22900	1764.3
1-Propanol	546127	676097.4	15688973	22900	2612.5
2-Butanol	238480	18653093.1	15688973	22900	464.4
1-Butanol	479889	709900.1	15688973	22900	3368.7
2-Pentanol	2105	19880.9	15688973	22900	0.4
1-Pentanol	104871	161930.9	15688973	22900	807.5
	MW	Weight (mg)	mmol_{sample}		
Methanol	32.04	45.522	1.421		
Ethanol	46.07	50.412	1.094		
2-Propanol	60.10	5.183	0.086		
1-Propanol	60.10	7.674	0.128	Total Oxygenate	
2-Butanol	74.13	1.364	0.018	Weight (mg) (based on	41.68
1-Butanol	74.13	9.895	0.133	sample volume)	
2-Pentanol	88.16	0.001	0.000	Total Oxygenate	
1-Pentanol	88.16	2.372	0.027	Weight (mg) (based on	122.42
Water	18.01	1907.577	105.918	total volume)	
				Weight Percent of	93.97
				Water	

Appendix VIII

Data for Oil Phase

for

Varied K Catalysts

6%Mo, 16%Fe, 0.8%Cu, 0.45%K

Injection Volume (µL)	0.1	Total Volume (µL)	650	Total Weight (mg)	400
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Correction factor	0.348281312
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Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	2.6966	79162	4.582	29.781	10.372	0.120	2.773
C ₇ (i-parafin)	100.23	1.1259	33051	1.631	10.600	3.692	0.037	0.987
C ₇ (parafin)	100.23	12.0123	352629	22.082	143.536	49.991	0.499	13.367
C ₇ (olefin)	98.21	0.9507	27909	1.302	8.461	2.947	0.030	0.788
C ₈ (i-parafin)	114.26	1.6777	49250	2.667	17.339	6.039	0.053	1.615
C ₈ (parafin)	114.26	16.9452	497437	31.350	203.772	70.970	0.621	18.977
C ₈ (olefin)	112.24	2.1884	64241	3.627	23.574	8.211	0.073	2.195
C ₉ (parafin)	128.29	14.6976	431457	27.127	176.327	61.411	0.479	16.421
C ₉ (olefin)	126.27	4.0899	120062	7.199	46.795	16.298	0.129	4.358
C ₁₀ (parafin)	142.32	10.9826	322400	20.148	130.962	45.612	0.320	12.196
C ₁₀ (olefin)	140.30	3.3841	99342	5.873	38.176	13.296	0.095	3.555
C ₁₁ (parafin)	156.35	7.2262	212129	13.091	85.092	29.636	0.190	7.924
C ₁₁ (olefin)	154.33	2.6167	76816	4.432	28.805	10.032	0.065	2.683
C ₁₂ (parafin)	170.38	3.5269	103535	6.141	39.920	13.903	0.082	3.718
C ₁₂ (olefin)	168.36	1.6949	49755	2.700	17.549	6.112	0.036	1.634
C ₁₃ (parafin)	184.41	2.0592	60450	3.384	21.998	7.661	0.042	2.049
C ₁₃ (olefin)	182.39	1.1531	33851	1.682	10.933	3.808	0.021	1.018
C ₁₄ (parafin)	198.44	1.5933	46774	2.509	16.309	5.680	0.029	1.519
C ₁₄ (olefin)	196.42	0.973	28562	1.344	8.733	3.042	0.015	0.813
C ₁₅ (parafin)	212.47	1.0505	30838	1.489	9.680	3.371	0.016	0.901
C ₁₅ (olefin)	210.45	0.7047	20687	0.840	5.457	1.901	0.009	0.508
Total				165.200	1073.797	373.984	2.960	100.000

6%Mo, 16%Fe, 0.8%Cu, 1.8%K

Injection Volume (µL)	0.1	Total Volume (µL)	2700	Total Weight (mg)	2210
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Correction factor	0.934201599
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Compound	MW	Weight Percent from GC	Area	Weight in injection (µg)	Weight in Sample (mg)	Corrected Weight in Sample (mg)	Amount in Moles (mmols)	Weight Percent
C ₆ (parafin)	86.20	2.3045	44673	2.375	64.113	59.895	0.695	2.715
C ₇ (parafin)	100.23	5.7927	112295	6.702	180.957	169.050	1.687	7.663
C ₇ (olefin)	98.21	5.6704	109923	6.550	176.858	165.221	1.682	7.490
C ₈ (parafin)	114.26	7.5219	145874	8.851	238.977	223.253	1.954	10.120
C ₈ (olefin)	112.24	6.2443	121049	7.262	196.083	183.181	1.632	8.304
C ₉ (parafin)	128.29	7.11	137831	8.336	225.080	210.270	1.639	9.532
C ₉ (olefin)	126.27	5.2576	101922	6.038	163.033	152.306	1.206	6.904
C ₁₀ (parafin)	142.32	6.0932	118120	7.075	191.022	178.453	1.254	8.090
C ₁₀ (olefin)	140.30	4.2579	82542	4.798	129.547	121.023	0.863	5.486
C ₁₁ (parafin)	156.35	4.8659	94329	5.552	149.913	140.049	0.896	6.349
C ₁₁ (olefin)	154.33	3.3168	64297	3.630	98.021	91.572	0.593	4.151
C ₁₂ (parafin)	170.38	2.2205	43045	2.270	61.300	57.267	0.336	2.596
C ₁₂ (olefin)	168.36	4.0998	79475	4.602	124.247	116.072	0.689	5.262
C ₁₃ (parafin)	184.41	2.9023	56262	3.116	84.138	78.602	0.426	3.563
C ₁₃ (olefin)	182.39	1.967	38131	1.956	52.809	49.335	0.270	2.236
C ₁₄ (parafin)	198.44	2.4899	48268	2.605	70.325	65.698	0.331	2.978
C ₁₄ (olefin)	196.42	1.4521	28150	1.317	35.563	33.223	0.169	1.506
C ₁₅ (parafin)	212.47	2.0013	38795	1.998	53.957	50.407	0.237	2.285
C ₁₅ (olefin)	210.45	1.1183	21680	0.903	24.384	22.780	0.108	1.033
C ₁₆ (parafin)	226.50	1.6147	31302	1.519	41.010	38.311	0.169	1.737
C ₁₆ (olefin)	224.48	0.8253	15999	0.540	14.568	13.609	0.061	0.617

C ₁₇ (parafin)	240.53	1.3213	25614	1.155	31.181	29.130	0.121	1.321
C ₁₇ (olefin)	238.51	0.5767	11180	0.231	6.241	5.830	0.024	0.264
C ₁₈ (parafin)	254.56	1.0708	20758	0.844	22.791	21.291	0.084	0.965
C ₁₈ (olefin)	252.54	0.4038	7829	0.017	0.451	0.421	0.002	0.019
C ₁₉ (parafin)	268.59	0.8594	16659	0.582	15.708	14.675	0.055	0.665
C ₂₀₊	282.62	2.2995	44579	2.369	63.951	59.743	0.211	2.708

Total	87.457	2361.339	2205.967	16.838	100.000
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