Catalytic Conversion of Biomass Derived Syngas to Liquid Fuels using Fischer-Tropsch Synthesis

Pratibha Sharma

Louisiana State University and Agricultural and Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

Part of the Chemical Engineering Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_theses/3193

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master's Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
CATALYTIC CONVERSION OF BIOMASS DERIVED SYNGAS TO LIQUID FUELS USING FISCHER-TROPSCH SYNTHESIS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agriculture and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

in

Department of Chemical Engineering

by

Pratibha Sharma
B. E, Panjab University, 2008
August 2013
ACKNOWLEDGEMENTS

I would like to express my gratitude towards my advisor Dr J.J Spivey, without whose guidance, constant support and motivation, this work would not have been possible. Under his mentorship and encouragement, I have learnt a lot and this knowledge would go a long way in shaping me as better researcher, engineer and a person. I would also like to thank Dr. Kerry Dooley and Dr. John Flake who were part of my committee and provided critical insight on my thesis.

This work was funded by the U.S. Department of Agriculture, under Award Number 11-DG-11221636-187. I would like to thank Tom Elder and Les Groom from United States Department of Agriculture for the support and motivation during my research. I sincerely thank my colleagues Devendra, Nitin, Miranda, Khiet and Zi for providing a great working environment. I would specially like to thank Miranda and Devendra for helping me to learn how to operate the laboratory equipment and performing data analysis. I would also like to thank Amie Hansel for her support and friendship which made time here a memorable one.

I would also like to thank Dr. Dooley at Louisiana State University for providing the adsorbents for the syngas cleaning. Without his help, I would not have been able to run the actual biomass derived syngas provided by USDA.

I would like to thank Ms. Wanda LeBlanc at Louisiana State University for helping in getting the XRD data, Mr. Thomas Beasley at Florida International University, for helping with the SEM and EDX experiments and Ms. Kim Hutchison at North Carolina State University for helping with the ICP analysis.
I would like to acknowledge Dr. Gary Jacobs at University of Kentucky, for the liquid sample analysis. Without his help, the complete analysis needed for the project would not have been possible.

I would also like to thank the faculty at LSU for guiding me through the courses and providing the knowledge to apply chemical engineering principles to problems and the staff at the Chemical Engineering Department especially Paul Rodriguez and Joe Bell for helping me with equipment related problems.

Finally, I would like to thank my family, whose unconditional love and support gave me the courage and motivation to succeed in life.
ACKNOWLEDGEMENTS............................................................................................................ ii

LIST OF TABLES......................................................................................................................... vi

LIST OF FIGURES ...................................................................................................................... vii

ABSTRACT ................................................................................................................................. viii

CHAPTER 1. INTRODUCTION AND LITERATURE REVIEW ............................................... 1
  1.1. Conversion of Biomass to liquid fuels through Fischer-Tropsch Synthesis .......... 2
  1.2. Gas cleaning and Preconditioning ................................................................. 4
  1.3. Fischer -Tropsch Synthesis ............................................................................ 5
    1.3.1. Reaction Chemistry ............................................................................... 7
    1.3.2. Different Fischer-Tropsch Catalysts .................................................... 9
    1.3.3. Effect of Chemical promoters on Fe based FT catalysts ..................... 10
    1.3.4. Effect of different structural promoters on Iron catalysts ................. 11
    1.3.5. Catalyst Pretreatment ................................................................... 13
  1.4. Research Objective ....................................................................................... 14

CHAPTER 2. EXPERIMENTAL ................................................................................................. 16
  2.1. Catalyst Preparation .................................................................................... 16
  2.2. Catalyst Characterization ........................................................................... 17
    2.2.1. X-Ray Diffraction ................................................................. 17
    2.2.2. BET Surface Area Measurement .................................................. 17
    2.2.3. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) 18
    2.2.4. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray
      (EDX) Analysis ................................................................. 18
    2.2.5. H2 Temperature Programmed Reduction (H2 TPR) ......................... 18
    2.2.6. CO Temperature Programmed Reduction (CO TPR) ......................... 19
    2.2.7. Temperature Programmed Hydrogenation (TPH) ............................ 19
    2.2.8. CO Temperature Programmed Desorption (CO TPD) ....................... 20
  2.3. Catalytic Performance Test ........................................................................... 21

CHAPTER 3. RESULTS AND DISCUSSION ............................................................................... 23
  3.1. Catalyst Characterization ............................................................................ 23
    3.1.1. X-Ray Diffraction ........................................................................... 23
    3.1.2. BET surface Area ........................................................................... 24
    3.1.3. Bulk composition analysis using ICP-OES ....................................... 25
    3.1.4. SEM and EDX ................................................................................. 25
    3.1.5. H2 Temperature Programmed Reduction (H2 TPR) ......................... 31
    3.1.6. CO Temperature Programmed Reduction (CO TPR) ......................... 33
    3.1.7. Temperature Programmed Hydrogenation (TPH) ............................ 35
    3.1.8. CO Temperature Programmed Desorption (CO TPD) ....................... 38
  3.2. Fischer-Tropsch Synthesis ........................................................................... 40
LIST OF TABLES

Table 3.1. BET surface area of the three catalysts................................................................. 25
Table 3.2. Bulk composition analysis of the catalysts using ICP-OES .............................. 25
Table 3.3. Quantitative H₂ Consumption during H₂ TPR of the Fe/Cu/K/Si, Fe/Cu/K/Al, Fe/Cu/K/Zn catalysts in 10% H₂/Ar. .............................................................. 32
Table 3.4. Temperature Programmed Hydrogenation results of carbonaceous species after pretreatment of catalysts in 5% CO/He. ................................................................. 37
Table 3.5. Amount of CO desorbed from catalyst surfaces during CO Temperature Programmed Desorption. .............................................................. 40
Table 3.6. Average carbon conversion and olefin/paraffin ratio of catalysts, Reaction condition: 300 °C, 2.8MPa, GHSV=1800 scc gcat⁻¹ h⁻¹ ................................................................. 43
Table A.3.1. GC settings for Gaseous Analysis ................................................................. 55
Table A.3.2. Temperature Program for Gaseous Analysis ................................................. 55
Table A.3.3. Average carbon conversion, product selectivity and olefin/paraffin ratio of catalysts, (GHSV=1800 scc gcat⁻¹ h⁻¹, P=2.8 MPa, T=300 °C) ................................. 56
LIST OF FIGURES

Figure 1.1. Thermochemical pathways to convert biomass to energy sources........................... 2

Figure 1.2. Flow diagram for conversion of Biomass to Transport quality fuels through Fischer-Tropsch reaction ................................................................................................................ 3

Figure 1.3. Carbide mechanism for CO Hydrogenation............................................................... 8

Figure 3.1. X-Ray Diffraction Spectra for the freshly calcined catalyst samples ....................... 23

Figure 3.2. XRD spectra of the post run catalysts ...................................................................... 24

Figure 3.3. SEM images of the catalysts samples- (a) Fe/Cu/K/Si, (b) Fe/Cu/K/Al, (c) Fe/Cu/K/Zn. .......................................................... 26

Figure 3.4. EDX profiles of the catalysts samples - (a) Fe/Cu/K/Si, (b) Fe/Cu/K/Al, (c) Fe/Cu/K/Zn .............................................................................. 27

Figure 3.5. EDX maps of Fe/Cu/K/Si-(a) Fe (b) Cu, (C) Si, (d) K. ............................................. 28

Figure 3.6. EDX maps of Fe/Cu/K/Si-(a) Fe (b) Cu, (C) Al, (d) K. ............................................ 29

Figure 3.7. EDX maps of Fe/Cu/K/Si-(a) Fe (b) Cu, (C) Zn, (d) K. ........................................... 30

Figure 3.8. Temperature Programmed Reduction of the catalysts in 10% H₂/Ar ......................... 31

Figure 3.9. CO₂ formation rate during CO Temperature Programmed Reduction of the catalysts in 5% CO/He ................................................................................................................. 34

Figure 3.10. TPH curves of the catalysts after activation in 5% CO/He (a) Fe/Cu/K/Si (b) Fe/Cu/K/Al (c) Fe/Cu/K/Zn. .......................................................... 36

Figure 3.11. CO Temperature programmed desorption from the carbided catalysts. ............... 39

Figure 3.12. Carbon Conversion on Fe/Cu/K/Si, Fe/Cu/K/Al, Fe/Cu/K/Zn catalysts with time on stream (GHSV=1800 scc gcat⁻¹ h⁻¹, P=2.8 MPa, T=300 °C) .......................................................... 41

Figure 3.13. Selectivity (C%) on Fe/Cu/K/Si, Fe/Cu/K/Al, Fe/Cu/K/Zn catalysts (GHSV=1800 scc gcat⁻¹ h⁻¹, P=2.8 MPa, T=300 °C) .......................................................... 42

Figure A.1. P & ID of the micro reactor .................................................................................. 53

Figure A.2. Operating conditions during Fischer-Tropsch Synthesis ....................................... 54
ABSTRACT

Biomass gasification and subsequent conversion to liquid hydrocarbons using Fischer-Tropsch synthesis is a promising source of energy in today’s scenario when the focus has shifted from conventional fuels to alternate sources of energy. Biomass derived syngas is different from other sources of syngas such as steam reforming of methane followed by water gas shift, in terms of H₂/CO ratio. Biomass syngas is usually hydrogen deficient and contains various impurities which need to be removed prior to Fischer-Tropsch Synthesis. Syngas derived from biomass also differs significantly with the different sources of biomass, gasification process and the cleanup conditions it is subjected to. The syngas used in this study has been produced by the air-blown, atmospheric pressure gasification of wood. The syngas from the gasification step is compressed and cleaned in a series of sorbents to produce the following feed to the F-T step: 2.78% methane, 11% CO₂, 15.4 % H₂, 21.3% CO and balance N₂. The relatively high level of CO₂, suggests the need to explore catalysts that are active for CO₂ hydrogenation as well is resistant to oxidation in presence of high levels of CO₂. Here we report the effect of three different structural promoters Si, Al and Zn on iron-based Fischer-Tropsch catalysts; specifically 100Fe/5Cu/4K/15Si, 100Fe/5Cu/4K/15Al and100Fe/5Cu/4K/15Zn. Although the effect of Si, Al or Zn on iron-based F-T catalysts has been examined previously in separate studies for CO+CO₂ hydrogenation, there is no direct comparison of these three structural promoters, nor any studies of these promoters for a syngas that has been directly derived from biomass and has a similar composition. In the present study, we found that catalysts promoted with Zn and Al showed higher extent of reduction and carburization and higher amount of carbides and CO adsorption as compared to Fe/Cu/K/Si catalyst, resulting in higher activity and selectivity to C₅+ hydrocarbons than the catalyst promoted with silica. The activity as measured by CO+CO₂ conversion was in
the order Zn>Al>Si. The Si-promoted catalyst had highest selectivity for methane and lower weight hydrocarbons.
CHAPTER 1. INTRODUCTION AND LITERATURE REVIEW

Due to increasing oil prices, depletion of fossil fuel reserves and increased environmental concerns, the focus has shifted from conventional fuels to alternate sources of energy. Biomass, though a less prevalent source, can be a source of clean energy. In recent times, biomass has been identified as one of the major supplement to the declining conventional energy resources[1]. Fuels derived from biomass are of great importance mainly because they have very low sulphur emissions [2, 3]. Also, if they are sustainably grown and consumed, they can have low lifecycle CO₂ emissions[4].

Biofuels can be obtained by either biochemical or thermochemical conversion of biomass. Biochemical methods include hydrolysis, esterification, and fermentation to produce fuels such as ethanol, biodiesel and biogas respectively[5]. The first generation biofuels like bioethanol and biodiesel are limited in production due to the high costs resulting from limited feedstock. Also, these fuels compete with agricultural industry over the availability of feedstocks and other economic factors such as land for cultivation, fertilizers, water and other resources that are required for the sustained growth of the feedstock for biofuels[4-6].

With increasing environmental concerns, shift of focus from conventional resources and limited availability of first generation biofuels, the second generation biofuels are needed. It is believed that biomass can provide one third of the world’s energy needs [6, 7]. This has led to the development of technology for harnessing the biomass energy. There are several routes for the production of biofuels through thermochemical means (1) direct combustion to produce heat, (2) gasification of biomass to produce syngas and subsequent catalytic conversion of biomass derived syngas to liquid fuels through Fischer Tropsch (FT) synthesis and (3)
pyrolysis/liquefaction of biomass to produce liquid fuels[4-7]. The different thermochemical pathways to convert biomass to energy are shown in Figure 1.1.

**Figure 1.1.** Thermochemical pathways to convert biomass to energy sources[1, 5]

1.1. **Conversion of Biomass to liquid fuels through Fischer-Tropsch Synthesis**

For converting biomass to liquid fuels, the biomass is first converted to syngas through the process of gasification. Gasification is the process of converting the organic raw material to gaseous mixtures of CO, CO₂, H₂ and CH₄ by reacting the raw material at high temperature without combustion[5]. Before gasification the raw feed is generally pretreated by grinding or drying [8]. Drying is one of the most critical steps in the biomass pretreatment, for obtaining high efficiency during gasification. It reduces the moisture content of the biomass to <15% [9].

Different synthesis gas compositions are obtained through different gasification methods such as atmospheric or pressurized, direct or indirect and air blown or oxygen blown[8]. Gasifiers are further classified as slagging/non slagging, fluidized bed or entrained flow and
fixed bed updraft or downdraft[10]. The flow diagram for the conversion of biomass to fuels is shown in figure 1.2.

Figure 1.2. Flow diagram for conversion of Biomass to Transport quality fuels through Fischer-Tropsch reaction[4, 5, 8, 10]
The gasification process is followed by cleaning of the syngas and conditioning. The process of gasification and subsequent cleaning usually requires almost 75% of the total investment cost in a biomass to liquid conversion process [10]. Thus, the choice of the gasifier is of critical importance to the Biomass to Liquid (BTL) conversion [4, 7, 10]. Gasification generally involves pyrolysis, char gasification and partial char combustion [11]. Tars are also produced during pyrolysis of the solid fuel in the temperature range of 400-800 °C along with CO, H₂, N₂, CH₄ and hydrocarbons. In gasification, the objective is to maximize gaseous products and minimize condensable hydrocarbons, tars and char by product [4, 7].

1.2. Gas cleaning and Preconditioning

Syngas from the gasification process usually contains impurities such as benzene, toluene, xylene (BTX) and other impurities such as NH₃, HCl, H₂S, HCN, COS, dust, soot ash, moisture and tars [1, 4, 5, 7, 8, 12]. These impurities may deactivate the Fischer-Tropsch catalyst over a period of time due to catalyst poisoning [8]. Thus, syngas cleaning is very critical for activity in Fischer-Tropsch Synthesis. The investment on gas cleaning generally depends on the economics of acceptance of production loss through catalyst deactivation [7].

Gasification produces large hydrocarbons called tars which condense under pressure. This may result in choking of the sorbent beds, as well as fouling of the downstream equipment. Tars may be removed by cracking either thermal or catalytic, which breaks the tars into smaller hydrocarbons [4, 10]. Also, tars can be removed by low temperature scrubbing using organic washing liquid [10]. The particulates in the syngas can be removed by ceramic or metal based filters. Other novel technologies for particulates removal include high performance nano membrane filters and particle agglomerating methods [5]. BTX can be removed by pressurizing
the gas to 6 bars, which removes the BTX completely[4]. For removing the inorganics, the syngas can usually be passed through the sorbent beds, the sorbent beds usually strip the alkali and sulphur compounds. The removal of sulphur is important because the sulphur adsorbs irreversibly on most catalysts and may thus deactivates the catalyst[4, 10]. Alkali contaminants in Fischer Tropsch process have different impact on both Iron (Fe) and Cobalt (Co) catalysts [7]. The design of sorbents and filters having high efficiency and reliability is of great importance to the Fischer-Tropsch (FT) Synthesis [5].

The syngas also contains large amounts of N₂, CO₂, CH₄ and low H₂/CO ratio [1, 4, 5, 7, 8]. The H₂/CO ratio can be a major factor for choosing the type of catalyst for FT reaction, and also the type of process[10]. Co catalysts usually demand high H₂/CO ratio while Fe catalysts can utilize syngas having a lower H₂/CO ratio. Steam reforming followed by water shift gas reaction of methane and light hydrocarbons over a Nickel (Ni) catalyst to CO₂ and H₂ is a typical process which can improve the overall H₂/CO ratio in the syngas, and the syngas can be adjusted to the desired H₂/CO ratio before feeding it to the FT reactor [10]. CO₂ can be removed from the syngas by absorption in amines [10].

1.3. Fischer -Tropsch Synthesis

In 1923, German Scientists Franz Fischer and Hans Tropsch, developed Fischer-Tropsch process by using alkalized Fe based catalysts to produce liquid hydrocarbons[1, 5]. Sasol in South Africa and Shell in Malaysia are two of the earliest commercial plants which are using Fischer-Tropsch Synthesis [13]. The discovery of large natural gas reserves could be one of the main driving forces for the utilization of Fischer-Tropsch technology for the conversion of syngas to transportation fuels.
Syngas for Fischer-Tropsch reaction can be derived from various sources such as coal, biomass and natural gas. Fischer-Tropsch synthesis has gained much importance due to its application in producing clean transportation fuels[14]. The products from this reaction depend on the source of syngas, type of reactor, temperature, pressure and type of catalyst used[15, 16]. Commercially, both gas-solid phase reactors and gas-liquid-solid phase reactors are being used for Fischer-Tropsch conversion.

Fischer-Tropsch (FT) synthesis can either be a low temperature or a High temperature process depending on the desired product distribution[17]. Low temperature FT process favors wax formation while high temperature FT process is generally used where middle distillate hydrocarbons or olefins are more desired[18]. FT temperatures are usually kept below 400 °C, as higher temperature favors methane formation [19]. The low temperature FT reactors are generally fixed bed or slurry type while for high temperature FT synthesis fixed bed, fluidized bed or circulating bed reactors can be used[15].

Fischer Tropsch reaction involves the conversion of CO and H₂ over a catalyst to long chain hydrocarbons[1, 5]. The basic equations which describe the FTS reaction are as follows[1, 14, 20]:

Main reactions

a. Paraffins:

\[ n\text{CO} + (2n+1)\text{H}_2 \rightarrow C_n\text{H}_{(2n+2)} + n\text{H}_2\text{O} \]

b. Olefins:

\[ n\text{CO} + 2n\text{H}_2 \rightarrow C_n\text{H}_{2n} + n\text{H}_2\text{O} \]

c. Water gas shift reaction[21]:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]
Side reactions

d. Alcohols:

\[ n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2}O + (n-1)\text{H}_2\text{O} \]

e. Boudouard reaction:

\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \]

where, \( n \) is a positive integer (average length of the chain)

One of the primary products in Fischer-Tropsch synthesis is water. As can be seen from the above equations, it is formed in all reactions, except the Boudouard reaction. Since, there is no volume change in the water gas shift reaction; pressure does not have much impact on this reaction.

Thermodynamically, the formation of methane and alkanes is preferred over alkenes and higher hydrocarbons, thus requiring rigorous process conditions for liquid hydrocarbon formation[14].

1.3.1. Reaction Chemistry

Previous literature has suggested that Fischer-Tropsch synthesis is a polymerization reaction consisting of the following steps in carbide mechanism[22, 23]:

a) Adsorption of the reactant (CO) on the catalyst surface
b) Chain initiation by CO dissociation on the catalyst followed by hydrogenation.
c) Chain propagation and growth by reaction of monomer (-CH\(_2\)-) with another monomer to form a higher hydrocarbon. The methylene species (-CH\(_2\)-) are formed when the dissociated CO molecule is hydrogenated by stepwise H\(_2\) addition. The probability of chain growth is termed as
α. Chain growth occurs due to sequential addition of methyl species to the growing alkyl chain which is attached to the catalytic surface.

d) Chain termination: Chain termination can happen at any stage to yield methane or olefins.

e) Desorption of the products from the catalytic surfaces.

Figure 1.3. Carbide mechanism for CO hydrogenation[22]

Secondary reactions also occur leading to the formation of oxygenates and paraffins.

Over the years other mechanisms have been proposed for FTS synthesis such as oxygenate mechanism, CO insertion mechanism and surface carbide mechanism. These mechanisms aim to
understand the different pathways through which different products and by products could be formed during FT synthesis[22].

1.3.2. Different Fischer-Tropsch Catalysts

The most active metals for FT synthesis are Ruthenium (Ru), Iron(Fe) and cobalt(Co) [24]. Other elements such as Ni, Rh, Ir, Pt and Pd are also used in Fischer-Tropsch Synthesis. However, their selectivity to C₅⁺ is lower than that of Ru, Co and Fe. Ru is an expensive metal, therefore making Fe and Co as the most viable option as an FT catalyst. Cobalt catalysts are generally considered more active than Iron catalysts [25] and they also have high stability [10]. Impregnation methods are usually employed for preparing cobalt catalysts. Different supports such as SiO₂, Al₂O₃, and TiO₂ etc. can be used as supports for cobalt catalysts. Generally cobalt catalysts are used where the H₂/CO ratio in the syngas is greater or equal to 2, as Co has negligible activity towards water gas shift reaction. Co catalysts are generally used for low temperature process where straight chain paraffin’s are the desired products [19].

Iron catalysts on the other hand are more flexible, and can be used for both High Temperature (HTFT) regimes (300-350 °C) and low temperature (LTFT) regimes (200-240 °C)[7]. Magnetite fusing is the catalyst preparation method for HTFT processes while LTFT catalysts are prepared by precipitation[15]. For a biomass derived syngas, Iron catalysts are usually preferred over Cobalt catalysts for FT synthesis as the H₂/CO ratio in biomass syngas is less than 1, and since iron is an active water gas shift catalyst, H₂ is produced during the reaction[26]. Also, where cost is a factor, Iron is preferred as it is cheaper and more versatile than Co [25].
1.3.3. Effect of Chemical promoters on Fe based FT catalyst

Many studies have been conducted to study the effect of alkali promotion on the performance of iron catalysts during Fischer-Tropsch Synthesis [27-29]. Ngantsoue-Hoc et al. in their study observed that CO conversion varied with different alkali promotion. At 20% conversion the activity followed the order Li=K>Na>un-promoted> Rb=Cs, while at a higher conversion the order was K> un-promoted>Na>Rb>Cs>Li[27]. In another study[30], the order was found to be Na>K>Li=Rb>un-promoted. It is believed that for iron based catalysts during FTS, chain growth probability increases with alkali promotion. The effect of Potassium loading has been extensively studied on iron catalysts[31, 32]. It has been observed that potassium promotion increases the catalytic activity and selectivity towards C$_5^+$ hydrocarbons. It also increases the WGS activity. However, high loading with potassium could lead to increased carbon deposition and subsequent deactivation of the catalyst[32]. K was found to suppress reduction of Fe$_2$O$_3$ in H$_2$ [33], however, it promoted reduction in CO[34, 35]. K promotion also decreased H$_2$ adsorption over a catalyst surface [35]. Promotion of iron based catalysts with K increases the activity and selectivity to higher hydrocarbons for CO$_2$ hydrogenation[36].

Iron catalysts for Fischer-Tropsch synthesis are also promoted with Copper (Cu). Copper facilitates the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ and subsequent reduction to metallic iron or iron carbides when reduced in H$_2$ or CO respectively. According to previous studies [31, 37, 38], presence of Cu decreases the reduction temperature of Fe$_2$O$_3$ to a much lower temperature, due to spillover of active hydrogen in case of H$_2$ reduction. Also, metallic Copper can withdraw oxygen atoms from other oxide phases which helps in reduction at lower temperature as in case of CO reduction[34]. Bukur et al. [39] observed that Cu alone can increase the FTS activity due to high activation and reduction of the catalyst, however Li et al[31] observed that Cu promotion
led to increase in the methane selectivity of the catalysts. Zhang et al. [34], found that Cu and K if present together in the catalyst have a synergistic effect which enhances reduction in either CO or H₂ and also improves the FTS and WGS activities.

1.3.4. Effect of different structural promoters on Iron catalysts

Different promoters like SiO₂, Al₂O₃, TiO₂ and MgO have been studied to determine their effect on the mechanical and attrition properties of iron based catalysts[40]. The structural promoters are added to increase the surface area, provide mechanical strength and reduce sintering of the catalysts under thermal treatments[36]. It has also been observed that the metal oxide promotion has great effect on activity and selectivity of the FT catalysts with different syngas compositions.

SiO₂ has been widely studied as a mechanical and structural promoter in many previous studies for CO hydrogenation [32, 41-43]. Incorporation of SiO₂ in the catalysts increases the surface area of the catalyst but leads to decrease in CO adsorption and catalytic activity. The decrease in reducibility and carburization is considered the reason for the decrease in activity on increasing the SiO₂ loading in the catalyst[42]. Dlamini showed that catalysts free of SiO₂ had higher activity than the catalysts in which SiO₂ was added[41]. For comparing SiO₂ and Al₂O₃ promoters for CO hydrogenation a study was conducted by Zhao et al where they studied the effect of potassium promotion on different structural promoters for conversion of CO to hydrocarbons. It was found that K promoted carburization in the order Al₂O₃>SiO₂>ZSM-5[44] and increased activity in the same order. Iglesia et al., found that Zn promotes CO hydrogenation, and acted as a structural promoter at Zn/Fe ratio of ~ 0.1, leading to an increase
in surface areas and inhibiting sintering of Fe oxide phases at low Zn contents, before and after thermal pretreatments[31].

Biomass derived syngas contains significant amount of CO₂. Thus CO₂ hydrogenation becomes critical to FT synthesis of this type of syngas. CO₂ hydrogenation over Fe based catalysts has been previously studies on Fe based catalysts [30, 45, 46]. In study by San-Sung et al. [46], iron based catalysts promoted with V, Mn, Cr and Zn were studied for CO₂ hydrogenation and Zn was found to promote CO₂ hydrogenation activity in comparison to other metals like V, Cr and Mn [46]. Prasad et al. [47] also found Zn promoted iron based catalysts to promote CO₂ hydrogenation as compared to Cr and Mn. In the same study, structural promoters such as SiO₂, TiO₂ Al₂O₃ were also tested for CO₂ hydrogenation. The study concluded that activity increased in the order Fe/Al₂O₃> FeTiO₂>Fe/SiO₂. According to Yan et al[48], Si addition to a Fe/Cu/K catalyst can weaken Fe and K interaction, while higher extent of carburization in case of Al promoted iron catalyst prepared by coprecipitation may result in increased activity and selectivity to higher hydrocarbons.

Most previous literature studying the effect of structural promoters is either on CO hydrogenation or CO₂ hydrogenation. Few studies have looked at the effect of structural promoters on hydrogenation of CO+CO₂ mixtures. Riedel et al. [30]studied the effect of SiO₂, TiO₂ and Al₂O₃ promoters for both CO₂ hydrogenation and CO+CO₂ gas mixture over Fe based catalysts. They found that the activity of Al₂O₃ promoted iron based catalyst was highest for a gas composition having H₂/CO₂ ratio of 3 in CO₂ hydrogenation. For CO+CO₂ syngas on Fe/K/Al₂O₃ catalyst, CO₂ conversion increased on increasing the content of CO₂ during the Fischer-Tropsch Synthesis. Riedel et al. also found that olefin selectivity increased with increasing the CO₂ content in the synthesis gas mixture. Also, it was observed that potassium
containing Al promoted catalysts adsorbed higher CO₂ than Si promoted catalysts[30]. In another study, model syngas with composition 11% CO, 32% CO₂, 5% Ar and 52% H₂ was tested with Fe/Cu/K/Al and Fe/Cu/K/Si catalysts[36]. It was found that Fe/Cu/Al/K had higher catalytic activity than Fe/Cu/K/Si catalysts due to the higher stability of the carbide containing iron phases. The study also concluded that the conversion of CO₂ to hydrocarbons in the CO+CO₂ mixture was almost negligible at low hydrogen content, but increased on increasing the H₂ content of the feed gas [36]. Iglesia et al. [49] in their study on Fe/Cu/K/Zn found that CO₂ addition to syngas does not influence CO₂ forward rates in water gas shift, but increases the reverse rate of water gas shift. Thus, CO₂ addition could decrease the net amount of CO₂ formation and increase oxygen removal as H₂O, leading to high olefin content and C₅⁺ selectivity in the products. Thus, based on previous literature[36], it can be said in presence of CO₂, other binders should be considered for improving the catalytic activity. Thus, for a biomass derived syngas rich in CO₂, the choice of a suitable catalyst can play a vital role in BTL economics.

1.3.5. Catalyst Pretreatment

The performance of a catalyst is dependent on the active metal phase during the reaction[20]. The catalysts produced after calcination generally exist in the oxide phase. It is therefore required to activate or pretreat the catalyst to obtain the phase which is catalytically active. Reduction of the iron based catalyst in H₂, CO or H₂/CO is usually believed to convert the Fe₂O₃ phase to the active metallic iron phase in case of H₂ reduction or iron carbide phase in case of CO or H₂/CO reduction[50]. Different iron phases such as metallic iron, Fe₅O₄, θ-Fe₃C, ε-Fe₂,2
C, χ-Fe₅C₂ have been found and the carbides are generally believed to be the active phases for FTS [20, 31, 51, 52].

1.4. Research Objective

The syngas being used in this study, is obtained by air blown gasification of biomass at the USDA facility in Pineville, and is fed to the reactor after cleaning. The composition of the syngas under study is 2.78% Methane, 11% CO₂, 15.4 % H₂, 21.3% CO, and balance N₂. Iron based catalysts are the preferred choice due to its ability to promote water gas shift activity for hydrogen deficient syngas[26]. Also, Cu and K promotion has synergistic effect on iron based catalysts during Fischer-Tropsch Synthesis, leading to an increase in the FTS and WGS activity[34]. These promoters are used in this research work.

The syngas under study is rich in CO₂. Many studies have been conducted in the past for the hydrogenation of CO₂ or CO hydrogenation of syngas rich in CO₂. During hydrogenation (i) CO₂ either reacts with H₂ and gets converted to methanol [53, 54], (ii) undergo reverse water gas shift reaction to produce CO which then undergoes subsequent Fischer-Tropsch Synthesis or (iii) it can directly hydrogenate to hydrocarbons[47]. CO₂ hydrogenation in FTS has been studied over Fe based catalysts as they are active in both water gas shift synthesis and reverse water gas shift synthesis and therefore are generally considered more suitable for CO₂ containing syngas [55-57]. Previous literature shows that CO hydrogenation in CO₂ rich environment requires a catalyst which has higher extent of carburization and is resistant to oxidation[30, 36]. Structural promotion of Fe/Cu/K is found to significantly affect catalytic activity and selectivity of CO₂ rich syngas in Fischer-Tropsch Synthesis based on previous studies[36, 58]. In this study iron based catalysts of the general composition 100Fe/5Cu/4K/15x where x is Si, Al or Zn have been
synthesized. Si, Al or Zn are added as structural promoters, and the objective of this research is to study the effect of these structural promoters on the physical and chemical characteristics of the catalysts, and also to study their effect on the activity and selectivity during Fischer-Tropsch synthesis of CO$_2$ containing syngas.
CHAPTER 2. EXPERIMENTAL

2.1. Catalyst Preparation

The catalysts were prepared by the technique of co-precipitation [59]. Base catalyst of 100Fe/5Cu/15x was prepared by co precipitating the aqueous solutions of the salts at constant pH, where x is Si, Al or Zn. In the process, 1.4 M solution of Fe(NO₃)₃•9H₂O (Aldrich 99.99%), and 3M solution of CuN₂O₆•3H₂O (Aldrich 99.99%) were first mixed together in deionized water. In a separate beaker Al(NO₃)₃.9H₂O (Aldrich 99.9%), Zn(NO₃)₂.6H₂O (Aldrich 99.99%) or tetraethylorthosilicate (Si(OC₂H₅)₄, Aldrich 99%) were dissolved in 40 ml of ethanol and stirred continuously. The solutions were then mixed together to a volume of 100 ml and heated to a temperature of 80 °C±3 °C. Alongside, 1 M solution of Ammonium carbonate ((NH₄)₂CO₃, Aldrich 99.999%) was also heated to a temperature of 80 °C±3 °C. The solutions were co-precipitated under vigorous mixing, and constant pH of 7-7.5 was maintained. After co-precipitation, the solution was allowed to age for 18 hours after which the pH was 8-9. The precipitate was filtered and washed until all the NH₃ left the precipitate and the pH was 7-8. After washing and filtering, the precipitate was dried in an oven at 120 °C for 24 hours. The dried precipitate was then crushed and sieved through 120 mesh and catalyst powder of particle size less than 125 microns was obtained.

The catalysts were further impregnated with Potassium Bicarbonate (KHCO₃) using incipient wetness impregnation method to obtain the final composition of 100Fe/5Cu/4K/15x.

The impregnated catalysts were calcined in a muffle furnace in flowing air. For calcination, the temperature was ramped at a rate of 5 degrees/min and the catalysts were calcined at a temperature of 350 °C for 5 hours in flowing air at a flow rate of 100ml/min. The
The furnace was cooled to room temperature at a rate of 5 degrees/min[60]. The catalysts were finally designated as Fe/Cu/K/Si, Fe/Cu/K/Al and Fe/Cu/K/Zn.

2.2. Catalyst Characterization

2.2.1. X-Ray Diffraction

For studying the crystalline nature of the catalyst using X-Ray diffraction, experiments were done on a Bruker/Siemens D5000 X-ray diffraction set up located in the Department of Geology at LSU. The instrumentation consisted of a ceramic X-ray tube with Cu Kα radiation which operated at a wave length of 1.54184 Å. The voltage for the X-Ray tube was 40 kV and the current was 30 mA. The setting of the anti-scatter slit was adjusted at 0.5°, while the angle of divergence slit for incident X-Ray beam was set at 1°. For analysis, the scan was done from 20° to 90° with a step size of 0.05 °/min. X-Ray diffraction was carried out for freshly calcined samples, as well as spent catalyst samples. For the XRD of the post run catalysts, the catalyst was first passivated. Passivation was required to ensure that the catalysts did not immediately oxidize on exposure to air after removing them for the reactor. 1% O₂/He at a flow rate of 30 ml/min was flown at room temperature for 1hr after pretreatment and post run. During passivation, the temperature increased by 5-8 °C, but returned to the normal temperature after a while. Proper passivation ensures that no more than a few nm of the catalyst surface gets oxidized when the catalyst is exposed to air.

2.2.2. BET Surface Area Measurement

For determining the Brunauer-Emmett-Teller (BET) surface area, N₂ physisorption at 77K was performed in AMI 200HP (Altamira instruments). BET surface area evaluation was
done for freshly calcined catalyst samples. Before physisorption, 0.05g of the sample was first heated in He to a temperature of 150 °C, to remove any moisture if present.

2.2.3. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

For determining the bulk elemental composition, ICP-OES was done at North Carolina State University on a Perkin Elmer 2000 DV instrument. The samples were first weighed to nearest 0.00001 g in a Teflon bottle, and 5 mL of aqua regia was added to each sample. The sample was allowed to sit overnight. 5 mL of HF was added to each sample and the samples were heated to ~ 95°C until they completely dissolved in HF. The volume was brought to 100 ml by adding deionized water. A blank analysis was also performed in the similar manner.

2.2.4. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis

Scanning Electron Microscopy (SEM) and Energy dispersive X-Ray (EDX) was done on freshly calcined catalysts to study the morphology and the elemental distribution and concentration of the external catalyst surface. The instrumentation for SEM and EDX was a JEOL JSM-5910-LV SEM with an EDAX UTW-Phoenix detector using Genesis software. The catalyst was uncoated and set up to run the elements selected for each group using the EDS spectrums for each material.

2.2.5. H₂ Temperature Programmed Reduction (H₂ TPR)

Temperature programmed reduction of catalysts in H₂ was done on Altamira (AMI 200 HP) instrument. 0.03 gm of a sample was placed in a quartz cell (6.5 inch (length) by 6 mm (outer diameter) by 4 mm (inner diameter)) and packed with quartz wool. The bed temperature
was measured continuously by a thermocouple which ran axially through the tube touching the quartz wool. Initially, the catalyst was oxidized completely by treating it with 10% O₂/He flowing at 50 ml/min. The temperature was ramped from room temperature to 400 °C at 5 °C/min and held for 30 min. The gas flow was switched to helium (He) and the catalyst was cooled to room temperature. 10% H₂/Ar was then allowed to flow at a rate of 30 ml/min, and the temperature was ramped at 5 °C/min to 950 °C. The signal was measured in a Thermal Conductivity detector (TCD). For calculating the amount of H₂ consumed, Silver Oxide (Ag₂O), amounts 0.1gm and 0.15gm were also reduced in H₂ similarly, and area calibration was done to calculate amount of H₂ consumed by the iron catalysts.

2.2.6. CO Temperature Programmed Reduction (CO TPR)

0.03 gm of the catalyst sample was placed in the quartz tube of the AMI 200 HP. The catalyst sample was completely oxidized under 10% O₂/He; the temperature was raised to 400 °C at a ramping rate of 5 °C/min and held at this temperature for 30 min. The catalyst sample was then cooled to ambient temperature in flowing He. After oxidation, the gas was switched to 5% CO/He at a flow of 50 ml/min and the temperature was increased to 950 °C at a ramping rate of 5 °C/min. The gas leaving the reactor was connected to a quadruple AMETEC Mass Spectrometer (MS) instrument, and the signal for CO and CO₂ was measured.

2.2.7. Temperature Programmed Hydrogenation (TPH)

TPH spectra were obtained after pretreating the catalyst in 5% CO/He. 100 mg of the catalyst was purged with helium to a temperature of 150 °C and then subsequently cooled to ambient temperature. The catalyst was pretreated in 5% CO/He flowing at 50 ml/min, at a
temperature of 280 °C, the temperature ramped at a rate of 5 °C/min and held there for 24 hrs. After pretreatment, the catalyst was cooled to 35 °C in flowing He. Subsequently the gas was switched to 50 ml/min of 10% H₂/Ar and the temperature was increased to 950 °C at a ramping rate of 5 °C/min. CH₄ signal was monitored in the Mass spectrometer (mass 15 was monitored instead of 16) to analyse the evolution of different carbon forms with temperature.

2.2.8. CO Temperature Programmed Desorption (CO TPD)

For CO TPD, 100 mg of the sample was loaded in the same quartz tube and the catalyst sample was treated with flowing He, temperature was increased to 150 °C, and held there for 30 min to ensure moisture removal. The sample was cooled to ambient temperature. The gas flow was then switched to 5% CO/He, at a flow rate of 30 cc/min and the temperature was raised to 280 °C at a ramping rate of 5 °C/min. The catalyst was held at this temperature for 6 hrs. After reduction and carburization, the gas flow was changed to He and allowed to flow through the catalyst at 280 °C for 30 min, to ensure complete removal of any adsorbed species from the catalyst surface. The temperature was then reduced to 35 °C in flowing He.

5% CO/He at a flow rate of 50 ml/min was allowed to flow over the catalyst for 30 min, while keeping the temperature constant. The gas flow was switched to He to flow over the catalyst till the CO baseline leveled off. TPD was done by flowing 30 ml/min of He over the catalyst, and the temperature was raised to 950 °C at a rate of 5 °C/min. The gas from the reactor was connected to the quadruple Mass Spectrometer through a capillary tube and the signal for CO & CO₂ was measured.
2.3. Catalytic Performance Test

Reactor system: Catalytic activity was measured in PID Micromeritics instrument. The system has the capability to condense and store higher hydrocarbons in a trap as liquid. Water is collected in a separate trap. The unconverted syngas along with lighter hydrocarbons (carbon number less than 6), and CO₂ exits the reactor at atmospheric pressure and can be analyzed in a gas chromatograph.

Syngas Cleaning: Before feeding the syngas to the reactor for FTS, the syngas was passed through a series of adsorbents and filters for removal of impurities, moisture and oxygen. The impurity levels for NH₃, HCL, and H₂S after the filters were checked using Kitagawa gas detector tubes.

Catalyst Pretreatment: 1 gm catalyst was diluted with 5 parts sand to avoid temperature gradients in the catalyst bed due to the exothermic nature of the reaction. The temperature was increased to 280 °C in flowing helium. After attaining the temperature of 280 °C, the gas flow was changed to 50% CO, balance helium at a total flow rate of 60 ml/min. The catalyst was reduced and carburized in 50% CO for 24 hrs. During the pretreatment the pressure was maintained at 1 bar.

Reaction: After activation, the reactor was flushed with He gas flowing at 50 ml/min for 1 hr. The gas was then switched to flow the syngas at a total GHSV of 1800 scc h⁻¹ gcat⁻¹ and the temperature was increased to 300 °C, and the pressure was increased to 2.8 MPa [61].

The run was allowed to continue for 144 hrs. The instrument has a peltier cell, which condenses the gases leaving the reactor. The peltier cell separating the liquid phase from the gases was maintained at temperature of 5 °C. The liquids were collected in a trap, while the uncondensed gases at atmospheric pressure were collected and analyzed in a Shimadzu GC-2014
gas chromatograph. The GC system consists of a FID (Flame ionization detector) used for analyzing hydrocarbons after being separated in a Restek Rt-Q-BOND column (23mx0.53mmx20µm). The wax trap was maintained at a temperature of 145 °C for collection of wax produced during the reaction.

The aqueous phase is analyzed in a Hewlett–Packard 5790A gas chromatograph with a Porapak Q packed column using a thermal conductivity detector. The oil phase is analyzed using a 6890 Agilent GC with a DB-5 capillary column and a flame ionization detector (FID). The wax phase is analyzed using 6890 Agilent GC FID with a high temperature DB-1 capillary column.
CHAPTER 3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

3.1.1. X-Ray Diffraction

The X-Ray Diffraction spectra for the three freshly calcined catalysts samples shown in Figure 3.1. shows that all catalysts are XRD amorphous[62], and any crystallite size is smaller than 4-5 nm based on the wavelength of the Cu Kα radiation[60]. This shows that the preparation method produced small, dispersed form of iron.

![X-Ray Diffraction Spectra](image)

**Figure 3.1.** X-Ray Diffraction Spectra for the freshly calcined catalyst samples

Similarly, the XRD spectra of the passivated post run catalysts shown in Figure 3.2. showed no peaks for any of the metal oxides of Fe, Cu, K, Al, Si or Zn. The catalyst during the
run was mixed with Quartz to eliminate thermal gradients. The peaks observed for all three catalysts are of Quartz, suggesting that the catalysts are XRD amorphous after reaction as well.

![XRD spectra of the post run catalysts](image)

**Figure 3.2.** XRD spectra of the post run catalysts

3.1.2. BET Surface Area

Table 3.1. gives the BET surface area of the three catalysts after calcination. Slightly higher catalyst surface areas than normal are obtained for all three catalysts, which is similar to the surface areas of the catalysts prepared by Lohitharn et al.[62] using the same preparation method. The catalyst containing Si has the highest surface area (428 m$^2$/g), which is in agreement with previous studies showing Si promoted catalysts to have higher surface areas than Al[36, 63].
### Table 3.1. BET surface area of the three catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Cu/K/Si</td>
<td>428</td>
</tr>
<tr>
<td>Fe/Cu/K/Al</td>
<td>360</td>
</tr>
<tr>
<td>Fe/Cu/K/Zn</td>
<td>276</td>
</tr>
</tbody>
</table>

3.1.3. Bulk composition analysis using ICP-OES

The bulk concentration of the catalysts as determined by ICP-OES presented in Table 3.2. corresponds to the target compositions of the atomic ratio of Fe/Me where Me is the promoter.

### Table 3.2. Bulk composition analysis of the catalysts using ICP-OES

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Fe</th>
<th>Cu</th>
<th>K</th>
<th>Si</th>
<th>Al</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
</tr>
<tr>
<td>Fe/Cu/K/Si</td>
<td>54.7</td>
<td>2.93</td>
<td>1.56</td>
<td>4.24</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Fe/Cu/K/Al</td>
<td>55.6</td>
<td>2.99</td>
<td>1.51</td>
<td>-----</td>
<td>4.26</td>
<td>-----</td>
</tr>
<tr>
<td>Fe/Cu/K/Zn</td>
<td>58.6</td>
<td>3.14</td>
<td>1.60</td>
<td>-----</td>
<td>-----</td>
<td>9.99</td>
</tr>
</tbody>
</table>

Max error: ±5%

3.1.4. SEM and EDX

SEM as represented by Fig 3.3. show that the catalyst particles size vary from 10-125µ. The catalyst particles are irregularly shaped for all catalysts, and different structural promoters did not change the catalyst morphology[62] which show uneven and faceted surfaces [60]. Since the catalysts are XRD amorphous, the SEM figures suggest that the catalyst particles
must be composed of many small iron oxide crystallites bound together but prevented from sintering together due to the presence of the structural promoters\[60, 62\]. It has been reported that Si prevents sintering of the catalyst\[64\], and acts as a binding agent \[65\], resulting in high surface areas, than catalysts which were prepared from precipitation of Fe without any Si \[66\]. The SEM and BET surface area for the Fe/Cu/K/Al and Fe/Cu/K/Zn suggest that Al and Zn like Si are acting as binding agents for the catalyst particles, preventing the catalysts from sintering and increasing the surface areas.

Figure 3.3. SEM images of the catalysts samples- (a) Fe/Cu/K/Si, (b) Fe/Cu/K/Al, (c) Fe/Cu/K/Zn
EDX profile of the three catalysts as shown in Figure 3.4. are point averaged and show that the atomic ratios of the Fe/Me where Me is Si, Al or Zn on the surface of the catalyst are similar for the three catalysts. The atomic ratios are Fe/Si~7.7, Fe/Al~7.8 and Fe/Zn~7.42, which are close to each other within the experimental error. These ratios are slightly higher than in the bulk.

**Figure 3.4.** EDX profiles of the catalysts samples- (a) Fe/Cu/K/Si, (b) Fe/Cu/K/Al, (c) Fe/Cu/K/Zn
EDX maps shown in Figure 3.5 for Fe/Cu/K/Si catalyst, Figure 3.6 for Fe/Cu/K/Al catalyst and Figure 3.7 for Fe/Cu/K/Zn catalyst, show that all elements are evenly distributed for all the catalysts, and Si, Zn and Al though in higher concentrations, do not interfere with the distribution of the other metals[60].

Figure 3.5. EDX maps of Fe/Cu/K/Si- (a) Fe (b) Cu, (C) Si, (d) K.
Figure 3.6. EDX maps of Fe/Cu/K/Al- (a) Fe (b) Cu, (C) Al, (d) K.
Figure 3.7. EDX maps of Fe/Cu/K/Zn- (a) Fe (b) Cu, (C) Zn, (d) K.
3.1.5. H₂ Temperature Programmed Reduction (H₂ TPR)

H₂ TPR of the three catalysts is shown in Figure 3.8. For the reduction of pure Fe₂O₃, two main peaks are observed at 330 °C and 530 °C. The first peak corresponds to the reduction of Fe₂O₃ to Fe₃O₄, while the second peak is assigned to the reduction of Fe₃O₄ to Fe. The two step reduction of Fe₂O₃ to Fe is as follows[39, 67].

\[3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}\]  \hspace{1cm} (i)

\[\text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O}\]  \hspace{1cm} (ii)

**Figure 3.8.** Temperature Programmed Reduction of the catalysts in 10% H₂/Ar.
Cu promotes the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ at lower temperatures than reduction of bulk Fe$_2$O$_3$ without any Cu [16, 31, 51, 68, 69]. Cu crystallites nucleate during reduction and provides H$_2$ dissociation sites giving reactive H$_2$, which reduces Fe$_2$O$_3$ at lower temperatures than catalysts without Cu [70, 71]. From the TPR of the catalysts; it is evident that pure Fe$_2$O$_3$ reduces to Fe$_3$O$_4$ at 330°C, while in the presence of Cu the catalysts reduce at a much lower temperature in the range of 205-244 °C.

For the catalyst Fe/Cu/K/Si, the first reduction temperature ~244 °C is higher than that for Fe/Cu/K/Al (~220 °C) and Fe/Cu/K/Zn (~205 °C). This may be attributed to better interaction of Cu with Fe$_2$O$_3$ in case of Fe/Cu/K/Al and Fe/Cu/K/Zn catalysts. This effect is more pronounced for Fe/Cu/K/Zn than Fe/Cu/K/Al. Previous studies have suggested that incorporation of SiO$_2$ and Al$_2$O$_3$ retards the reduction of iron oxide due to strong metal-support interactions[39, 72]. The quantitative H$_2$ consumption for reduction is presented in Table 3.3.

**Table 3.3. Quantitative H$_2$ Consumption during H$_2$ TPR of the Fe/Cu/K/Si, Fe/Cu/K/Al, Fe/Cu/K/Zn catalysts in 10% H$_2$/Ar**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Theoretical* H$_2$ consumption (mmol H$_2$/gcat)</th>
<th>Experimental H$_2$ consumption (mmol H$_2$/gcat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Cu/K/Si</td>
<td>5.58</td>
<td>5.69±0.14</td>
</tr>
<tr>
<td>Fe/Cu/K/Al</td>
<td>5.67</td>
<td>5.54±0.12</td>
</tr>
<tr>
<td>Fe/Cu/K/Zn</td>
<td>5.98</td>
<td>5.47±0.06</td>
</tr>
</tbody>
</table>

*Theoretical Consumption is based on ICP composition of the catalysts in Table 3.2. assuming reduction to Fe and Cu.
For the second stage reduction i.e Fe$_3$O$_4$ to Fe (eq (ii)), Fe/Cu/K/Zn is further reduced at lower temperature. This could be either due to better interaction with Cu or low interaction of Fe with Zn as structural promoter. For Fe/Cu/K/Al, the temperature for the second peak shifts to a higher temperature. The reduction of Fe in presence of Al at a higher temperature may be attributed to a strong interaction of Fe and Al$_2$O$_3$ [73], leading to a shift to higher temperature for the reduction of Fe$_3$O$_4$ to Fe.

3.1.6. CO Temperature Programmed Reduction (CO TPR)

CO TPR results are shown in Figure 3.9. During CO temperature reduction, the oxygen removal from the lattice is followed by carbon introduction in the lattice to form iron carbides[31]. This occurs in two steps both of which produce CO$_2$[74]:

$$3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$$\hspace{1cm}eq (iii)

$$\text{Fe}_x\text{O} + 2\text{CO} \rightarrow \text{Fe}_x\text{C} + 2\text{CO}_2$$\hspace{1cm}eq (iv)

In equation (iv), oxygen removal and carbon introduction occurs in the same step[20]. Also, during reduction CO$_2$ could be formed by the Boudard reaction:

$$2\text{CO} \rightarrow \text{C} + \text{CO}_2$$\hspace{1cm}eq (v)

The CO TPR of the catalysts shows three peaks. Fe$_2$O$_3$ is reduced to Fe$_3$O$_4$ in the temperature range of 150-250 °C. In the temperature range of 260 °C- 405 °C, Fe$_3$O$_4$ concurrently gets reduced and carburized to iron carbides ($\chi$-carbides)[31]. Above 405° C, transformation of the various iron carbides to stable carbide phases like cementite (Fe$_3$C) takes place [71]. Also above 405 °C, CO$_2$ formations occurs via the Boudard reaction[31]. This CO disproportionation causes excess amorphous carbon on the catalyst.
Figure 3.9. CO$_2$ formation rate during CO Temperature Programmed Reduction of the catalysts in 5 % CO/He.

For Fe/Cu/K/Zn the first peak for the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$ is at a temperature of 185 °C, while the first peak shifts to higher temperature with Al (~205 °C) and Si (~220 °C) promotion. Also, the concurrent reduction and carburization of Fe$_3$O$_4$ for Fe/Cu/K/Zn takes place at a slightly lower temperature than Fe/Cu/K/Al or Fe/Cu/K/Si. This second peak temperature is 310 °C for Zn promoted catalyst while the peak shifts to ~ 330 °C for both Si and Al promoted catalysts. The peak area is highest for Fe/Cu/K/Zn suggesting that more CO is consumed during this reduction and carburization process with less CO consumed for Fe/Cu/K/Al and even less for Fe/Cu/K/Si. This indicates that the catalyst promoted with Si is least carburized. The third
peak for the subsequent inter transition of iron carbides to more thermally stable carbides, and CO₂ formation due to the Bouduard reaction as shown in the CO TPR curves is also minimum in case of Fe/Cu/K/Si. Thus, it can be concluded that carburization increases in the order of Fe/Cu/K/Zn>Fe/Cu/K/Al>Fe/Cu/K/Si as judged by the CO TPR

3.1.7. Temperature Programmed Hydrogenation (TPH)

The catalyst composition changes during pretreatment and during the reaction run[75]. The iron catalyst undergoes phase transformations during activation, with Fe₂O₃ converted to Fe₃O₄, which is then transformed to iron carbides [76-79]. It is believed that carbide formation is required for the activity of the iron catalysts[80, 81], which are considered the active sites. Bartholomew et al. used TPH of carbided catalysts to study the different metal carbides and carbon species formed during pretreatment or during FTS reaction for both supported and unsupported catalysts[52].

Bartholomew et al. reported a method of analyzing the spectra qualitatively and quantitatively by deconvoluting the overlapping peaks and fitting them using Gaussian curves [52, 79]. The peaks in Fig 3.10. have been designated as α (adsorbed, atomic carbon, surface carbide), β (polymeric, amorphous aggregates), γ₁ (iron carbide: ε-Fe₂.0₂C), γ₂ (iron carbide-χ-Fe₂.₅C), δ₁ (semi ordered sheets) and δ₂ (moderately ordered sheets) based on the peak temperatures from Bartholomew et al. [52, 79, 82]
Figure 3.10. TPH curves of the catalysts after activation in 5% CO/He (a) Fe/Cu/K/Si (b) Fe/Cu/K/Al (c) Fe/Cu/K/Zn
For each catalyst, spectra of overlapping peaks are obtained. The curves have been deconvoluted using Gaussian curves and the equivalent peak temperatures and areas are shown in Table 3.4.

Table 3.4. Temperature Programmed Hydrogenation results of carbonaceous species after pretreatment of catalysts in 5% CO/He

<table>
<thead>
<tr>
<th>Catalyst Name</th>
<th>Type of carbon species</th>
<th>Peak Temperature (°C)</th>
<th>Carbon content (µg/mgcat)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Cu/K/Si</td>
<td>α</td>
<td>385</td>
<td>2.9</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>429</td>
<td>1.3</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>γ₁</td>
<td>508</td>
<td>19.6</td>
<td>79.5</td>
</tr>
<tr>
<td></td>
<td>γ₂</td>
<td>608</td>
<td>0.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Fe/Cu/K/Al</td>
<td>α</td>
<td>374</td>
<td>4.4</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>420</td>
<td>11.8</td>
<td>23.2</td>
</tr>
<tr>
<td></td>
<td>γ₁</td>
<td>547</td>
<td>29.9</td>
<td>59.0</td>
</tr>
<tr>
<td></td>
<td>γ₂</td>
<td>633</td>
<td>4.6</td>
<td>9.1</td>
</tr>
<tr>
<td>Fe/Cu/K/Zn</td>
<td>α</td>
<td>387</td>
<td>7.2</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>498</td>
<td>8.1</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>γ₁</td>
<td>591</td>
<td>18.0</td>
<td>34.0</td>
</tr>
<tr>
<td></td>
<td>γ₂</td>
<td>629</td>
<td>19.7</td>
<td>37.1</td>
</tr>
</tbody>
</table>

The temperature for the more intense peaks increases with Al and Zn promotion (500-700 °C). No graphitic carbon was observed during the TPH of the pretreated catalysts. It is evident from the carbon content obtained that carburization increases in the order of Zn>Al>Si. Based on studies by Bartholomew et al.[52, 79, 82], γ₁ carbon was assigned as ė-Fe₂.₂C and γ₂ carbon was assigned as χ-Fe₂.₅C (Hagg carbide). The thermal stability of the carbide is in the order ė<χ<θ (θ is the graphitic carbon not observed during pretreatment), because of increase in Fe-C bond strength. Based on the area under the curves and temperature assignment of the peaks from
previous literature [52, 75, 83] we find that $\alpha$-carbon (the most reactive carbon form) increased in the order of Zn>Al>Si. Higher content of $\alpha$ carbon can result in increased initial higher activity of the catalyst[84]. During pretreatment or reaction some part of the atomic surface carbon is converted to a polymeric form of amorphous, condensed $\beta$ carbon of moderate reactivity[52]. $C_{\alpha}$ can also condense to $C_{\delta}$ form of carbon which is graphitic carbon films having very low reactivity. $\beta$ carbon for the catalysts under study increases in the order Al>Zn>Si, while the total amount of carbides ($\gamma_1+\gamma_2$) is highest for Fe/Cu/K/Zn and lowest for Fe/Cu/K/Si. This can be attributed to increased CO content on the catalyst surface[75]. Also the amount of carbides ($\gamma_1+\gamma_2$) increases in the order of the increased reduction and carburization of the catalysts in CO which is Fe/Cu/K/Zn>Fe/Cu/K/Al>Fe/Cu/K/Si[75], and the content of thermally more stable carbides also increases in the same order. No graphitic carbon was observed during the pretreatment of the catalyst in 5% CO/He.

3.1.8. CO Temperature Programmed Desorption (CO TPD)

CO TPD is used to analyze the effect of Si, Al and Zn promotion on CO adsorption behavior of the catalysts. CO TPD curves are presented in figure 3.11. For Fe/Cu/K/Si, the desorption temperatures are in the temperature range 300-600 °C, with peaks at 410 °C and 555 °C, while for the Fe/Cu/K/Al the desorption occurs from a broad peak in the temperature range of 350-700 °C with a peak temperature of 510 °C. For the Fe/Cu/K/Zn catalyst, desorption temperature are in the range of 350-750 oC with two different peaks at 455 °C and 630 °C and a small shoulder at 685 °C.
Figure 3.11. Temperature Programmed Desorption of CO from the carbided catalysts

Desorption temperatures are lowest for Fe/Cu/K/Si with peaks at 410 °C and 555 °C. For Fe/Cu/K/Al catalyst, desorption peak shifts to a higher temperature and the desorption spectra shows a multi-peak overlapped curve with a peak temperature at 510 °C. Studies have been done previously on the desorption of CO from clean Fe (100) surfaces [85-88]. These studies suggest that CO desorbs from a Fe (100) surface from four peaks, three of which are attributed to desorption of molecular CO at temperature of −23, 67, and 157 °C, while the fourth peak at ~527 °C is ascribed to desorption of dissociative CO[89]. The desorption temperature of CO in this study from carburized surfaces are higher than those of molecular CO on Fe (100) surface.
and closer to the desorption temperature of dissociative CO ~ 527 °C[89, 90] in case of Fe/Cu/K/Al. Also based on previous studies, the required desorption temperature of CO from Fe₅C₂ surfaces is about 500 °C[89, 91]. The higher desorption temperature of 630 °C and small shoulder at 685 °C for Fe/Cu/K/Zn catalyst could result from the strongly bound CO on iron carbide surfaces[89]. From the area under the curves in Table 3.5., we see that CO adsorption is highest on Fe/Cu/K/Zn and least for Fe/Cu/K/Si. CO TPD results correlate with TPH and CO – TPR results as higher extent of reduction and carburization promotes stronger and more CO adsorption which can be seen from the CO TPD of the catalysts.

**Table 3.5.** Amount of CO desorbed from catalyst surfaces during CO Temperature Programmed Desorption

<table>
<thead>
<tr>
<th>Catalyst Name</th>
<th>Amount of CO desorbed (µmol/gcat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Cu/K/Si</td>
<td>235.58</td>
</tr>
<tr>
<td>Fe/Cu/K/Al</td>
<td>349.43</td>
</tr>
<tr>
<td>Fe/Cu/K/Zn</td>
<td>529.79</td>
</tr>
</tbody>
</table>

### 3.2. Fischer-Tropsch Synthesis

The effect of Si, Al and Zn promotion on Fe/Cu/K based catalysts for CO+CO₂ conversion as a function of reaction time is shown in Figure 3.12. For calculating conversion, the possibility of products being formed from both CO and CO₂ must be considered. CH₄ present in the reactant gas mixture is assumed to be inert. CO₂ can either undergo reverse water gas shift to CO and subsequently undergo Fischer-Tropsch synthesis, or directly hydrogenate to
hydrocarbons or react with H₂ to form methanol[47, 53, 54]. Therefore overall carbon conversion is calculated for the three catalysts using the equation:

\[
\text{Carbon conversion} = \frac{\text{moles}(\text{CO} + \text{CO}_2)_{\text{in}} - \text{moles}(\text{CO} + \text{CO}_2)_{\text{out}}}{\text{moles} (\text{CO} + \text{CO}_2)_{\text{in}}}
\]

The carbon conversion as seen from Figure 3.12. is highest for Fe/Cu/K/Zn catalyst, while it is lowest for Fe/Cu/K/Si. Iron carbides are generally believed to be the active sites for Fischer-Tropsch synthesis [35, 92-94]. Based on TPH of carbided catalysts, iron carbide formation follows the sequence Zn>Al>Si. Fig 3.12 shows that activity of the catalysts follow similar trend as the amount of carbides[93]. This shows a clear correlation between the extent of carburization and catalytic activity, which is consistent with previous studies correlating activity and extent of carburization [31, 61, 90].

**Figure 3.12.** Carbon conversion on Fe/Cu/K/Si, Fe/Cu/K/Al, Fe/Cu/K/Zn catalysts with time on stream (GHSV=1800 scc gcat⁻¹ h⁻¹, P=2.8 MPa, T=300 °C)
Figure 3.13. shows that methane selectivity decreases in the order Fe/Cu/K/Zn<Fe/Cu/K/Al<Fe/Cu/K/Si. Literature shows that enhanced CO adsorption leads to higher surface coverage of carbon species thus facilitating chain growth and enhanced selectivity to heavier hydrocarbons[95].

![Figure 3.13. Selectivity (C %) on Fe/Cu/K/Si, Fe/Cu/K/Al, Fe/Cu/K/Zn catalysts (GHSV=1800 scc gcat⁻¹ h⁻¹, P=2.8 MPa, T=300 °C)](image)

Based on CO TPD results, we know that CO adsorption increases in the order Fe/Cu/K/Zn > Fe/Cu/K/Al > Fe/Cu/K/Si. The selectivity results in Figure 3.13. show that selectivity towards higher hydrocarbons (C₁₉⁺) is highest for Zn while selectivity towards
methane and C₂-C₄ is suppressed. Selectivity towards methane and C₂-C₄ is highest for Fe/Cu/K/Si, while selectivity towards heavier hydrocarbons is suppressed. Additionally olefin/paraffin ratio is improved with the promotion by Al and Zn as can be seen from the results in Table 3.6.

Table 3.6. Average carbon conversion and olefin/paraffin ratio of catalysts, Reaction condition: 300 °C, 2.8MPa, GHSV=1800 scc gcat⁻¹ h⁻¹

<table>
<thead>
<tr>
<th></th>
<th>Fe/Cu/K/Si</th>
<th>Fe/Cu/K/Al</th>
<th>Fe/Cu/K/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO+CO₂ Conversion (%)</td>
<td>12.98</td>
<td>25.19</td>
<td>33.69</td>
</tr>
<tr>
<td>Olefins/n-Paraffins</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅⁻⁻C₁₁ / n-C₅-C₁₁</td>
<td>1.76</td>
<td>1.92</td>
<td>2.18</td>
</tr>
<tr>
<td>C₁₂⁻⁻C₁₈ / n-C₁₂-C₁₈</td>
<td>0.79</td>
<td>0.84</td>
<td>0.96</td>
</tr>
<tr>
<td>ASF (α)²</td>
<td>0.75</td>
<td>0.82</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Reaction condition: 300 °C, 2.8 MPa, GHSV=1800 scc gcat⁻¹ h⁻¹
²Calculated using C₇⁻⁻C₁₅ region of the plot

The chain growth probability (α) of a hydrocarbon chain formed by stepwise addition of C₁ intermediates is known as the Anderson Schulz Flory (ASF) distribution[96]. The equation for the ASF growth probability is given by [96]

\[ \log \left( \frac{W_n}{n} \right) = n \log(\alpha) + \text{constant} \]

where \( W_n \) is the weight fraction of the hydrocarbon with carbon number \( n \). The growth probability \( \alpha \) can be calculated from the slope of the curve.

From Table 3.6., it is evident that the growth probability \( \alpha \) also increases in the order Zn>Al>Si. Collectively these results indicate that chain propagation and selectivity to heavier hydrocarbons is increased with Al and Zn promotion in comparison to promotion of Fe/Cu/K with Si.

Co-precipitated Fe/Cu/K/Si catalysts have been often employed for commercial Fischer-Tropsch Synthesis. However for CO₂ rich feed, previous studies have suggested [30, 36, 48], that
a catalyst resistant to oxidation by CO₂ rich environment is required. The characterization results show that Si suppresses reduction in CO, has low amount of carbide formation and suppresses CO adsorption. These results are consistent with low activity of the catalyst along with high selectivity to methane and low selectivity to heavier hydrocarbons. Promotion with Zn and Al, however, enhance reduction in CO, carbide formation and CO adsorption as compared to Fe/Cu/K/Si catalyst resulting in high activity and selectivity to heavier hydrocarbons for the Zn or Al promoted Fe/Cu/K catalysts. According to literature, the correlation between activity for a CO₂ rich syngas on structural promoters is dependent on the different interaction between Fe and a structural promoter[36]. Yan et al. [48] in study on CO₂ hydrogenation reported that silica addition to Fe/Cu/K reduces the Fe and K dispersion on Si, while Al promotion enhances carburization. Jun et al.[36] also compared Si and Al structural promoters on iron based catalysts for CO +CO₂ hydrogenation and found that alumina as a structural promoter gave higher activity for hydrocarbon production than silica and had higher selectivity towards higher hydrocarbons. These results are consistent with our study. Jun et al also suggested that Al₂O₃ containing catalyst is easily carburized than Si containing catalyst, thus making the catalyst more resistant to oxidation in CO₂ rich environment. Based on the results in this study, it can be concluded that Fe/Cu/K/Zn is also carburized to a greater extent making it resistant to oxidation in the presence of CO₂ in the feed gas leading to higher activity and selectivity to higher hydrocarbons.
CHAPTER 4. CONCLUSIONS

Promotion of Fe/Cu/K catalyst with Si, Al or Zn greatly affects the reduction of the catalyst in H₂ and CO, CO adsorption, and carburization behavior as well the activity and selectivity in Fischer-Tropsch Synthesis. The co-precipitation method used to prepare catalyst resulted in XRD amorphous material. The catalyst promoted with Si has the highest BET surface area while incorporation of Al and Zn reduces the surface area. Reduction in CO is increased for Fe/Cu/K/Zn and Fe/Cu/K/Al as compared to Fe/Cu/K/Si. The high extent of reduction, carburization and CO adsorption for Fe/Cu/K/Zn catalyst resulted in high catalytic activity and resistance to oxidation of the catalyst in presence of CO₂ rich feed. Fe/Cu/K/Zn also shows lowest selectivity to methane formation and increased selectivity to higher hydrocarbons due to high surface coverage of carbon species from enhanced CO adsorption. Fe/Cu/K/Si catalyst however had low extent of carburization and less CO adsorption resulting in reduced catalytic activity, high selectivity to methane and low selectivity to heavier hydrocarbons. These results suggest that Fischer-Tropsch synthesis of biomass derived syngas rich in CO₂ requires a catalyst which is carburized to a higher extent, leading to higher resistance to oxidation in CO₂ rich environment.
REFERENCES


APPENDIX

A.1. Process and Instrumentation diagram of the micro reactor

Figure A.1. P & ID of the micro reactor
A.2. Program for Fischer-Tropsch reaction

![Image](https://via.placeholder.com/150)

**Figure A.2.** Operating conditions during Fischer-Tropsch Synthesis

A.3. Analysis of light gases

For this analysis a Shimadzu GC-2014 gas chromatograph was used. The GC system consists of a FID (Flame ionization detector) used for analyzing hydrocarbons after being separated in a Restek Rt-Q-BOND column (23mx0.53mmx20µm)
Table A.3.1. GC settings for Gaseous Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Oven temperature</td>
<td>40 °C</td>
</tr>
<tr>
<td>Detector (FID) temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>LTCD Temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>RTCD Temperature</td>
<td>250 °C</td>
</tr>
<tr>
<td>SPL Temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium</td>
</tr>
<tr>
<td>Total Flow (ml/min)</td>
<td>51.6</td>
</tr>
<tr>
<td>Column Flow (ml/min)</td>
<td>8.43</td>
</tr>
<tr>
<td>Purge Flow (ml/min)</td>
<td>1.00</td>
</tr>
<tr>
<td>Split ratio</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The FID and TCD were calibrated for lighter hydrocarbons and CO₂, CO and H₂ using standards for both low and high concentrations.

Table A.3.2. Temperature Program for Gaseous Analysis

<table>
<thead>
<tr>
<th>Rate (°C/min)</th>
<th>Temperature (°C)</th>
<th>Hold time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>175</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>250</td>
<td>5</td>
</tr>
</tbody>
</table>
A.4. Carbon Conversion, product selectivity and olefin/paraffin ratio of catalysts

Table A.3.3. Average carbon conversion, product selectivity and olefin/paraffin ratio of catalysts, (GHSV=1800 scc gcat⁻¹ h⁻¹, P=2.8 MPa, T=300 °C)

<table>
<thead>
<tr>
<th></th>
<th>Fe/Cu/K/Si</th>
<th>Fe/Cu/K/Al</th>
<th>Fe/Cu/K/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO+CO₂ Conversion (%)</td>
<td>12.98</td>
<td>25.19</td>
<td>33.69</td>
</tr>
<tr>
<td>HC distribution (C %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>19.5</td>
<td>10.2</td>
<td>8.5</td>
</tr>
<tr>
<td>C₂-C₄</td>
<td>32.3</td>
<td>28.0</td>
<td>26.3</td>
</tr>
<tr>
<td>C₅-C₁₁</td>
<td>15.5</td>
<td>20.4</td>
<td>18.5</td>
</tr>
<tr>
<td>C₁₂-C₁₈</td>
<td>4.4</td>
<td>11.7</td>
<td>13.9</td>
</tr>
<tr>
<td>C₁₉⁺</td>
<td>1.51</td>
<td>1.84</td>
<td>4.56</td>
</tr>
<tr>
<td>Oxygenates</td>
<td>2.0</td>
<td>1.03</td>
<td>0.84</td>
</tr>
<tr>
<td>Olefins/n-Paraffins</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅-C₁₁ /n-C₅-C₁₁</td>
<td>1.76</td>
<td>1.92</td>
<td>2.18</td>
</tr>
<tr>
<td>C₁₂-C₁₈ /n-C₁₂-C₁₈</td>
<td>0.79</td>
<td>0.84</td>
<td>0.96</td>
</tr>
<tr>
<td>ASF (α)ᵃ</td>
<td>0.75</td>
<td>0.82</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Reaction condition: 300 °C, 2.8 MPa, GHSV=1800 scc gcat⁻¹ h⁻¹
ᵃCalculated using C₇-C₁₅ region of the plot
VITA

Pratibha Sharma was born in 1986, Etah, Uttar Pradesh, India. She completed her High School education from Chandigarh, after which she joined Department of Chemical Engineering and Technology at Panjab University, Chandigarh, India in 2004 for her bachelors. She earned her Bachelors of Engineering with Honors in 2008. After that, she worked as a Process Engineer with Indian Oil Corporation Limited for three years from 2008-2011. In Aug’2011, she was admitted to Department of Chemical engineering, Louisiana State University. She worked under Dr. James Spivey as her research advisor at LSU. She completed her research in June’2013 and this thesis completes the requirement to obtain her Master’s Degree from Louisiana State University.