UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF BIMETALLIC CATALYSTS SUPPORTED ON ACTIVATED CARBON FOR FISCHER-TROPSCH REACTION

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By

AHMED SHAMIL ABDULRAHMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

January 2019

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DEDICATION

My beloved parents,

My wife

For their endless encouragement, patience, and support

And for being a great source of motivation and inspiration

And all my friends

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

SYNTHESIS OF BIMETALLIC CATALYSTS SUPPORTED ON ACTIVATED CARBON FOR FISCHER-TROPSCH REACTION

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January 2019

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Fischer-Tropsch Synthesis (FTS) is a process to convert a mixture of H_2 and CO synthesized gas generated from biomass gasification into high quality clean fuel with low sulfur content under the existence of metal catalysts. It is believed that the incorporation of two FT active metals with high surface area and weak metal-support interaction substrate such as AC would enhance the catalytic activity and improve gasoline fraction selectivity.

In this study, FT reaction was investigated in a tubular fixed bed reactor on two groups of prepared Co-Fe and Co-Ni catalysts supported by AC. The catalysts were synthesized by wet impregnation method and were characterized using high-end instrumental analysis for the morphology and physical properties of the catalysts. The incorporation of a second metal component into the catalyst has significantly modified the bimetallic catalyst properties leading to enhanced catalytic activity in FT reaction.

Maximum gasoline selectivity of 63 % and 69 % were achieved on the best bimetallic catalysts namely 10Co5Fe/AC and 7Co7Ni/AC, respectively. Temperature increase from 220 °C to 300 °C enhanced gasoline selectivity from 63 % to 88 % and 69 % to 92 %. In addition, carbon monoxide (CO) conversion increased from 46 % to 72 % and 43 % to 65 % on both bimetallic 10Co5Fe/AC and 7Co7Ni/AC catalysts, respectively. On the contrary, increased reaction pressure from 1 bar to 9 bar decreased gasoline selectivity from 88 % to 22 % and 92 % to 36 % but increased CO conversion from 72 % to 97 % and 65 % to 84 % on both bimetallic 10Co5Fe/AC and 7Co7Ni/AC catalysts. The optimum reaction conditions were considered based on the maximum selectivity of gasoline which was 300 °C reaction temperature and 1 bar reaction pressure. A decrease in gasoline selectivity of 42 % and 27 % as well as a decrease in CO conversion of 56 % and 34 % was noticed on both bimetallic catalysts

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10Co5Fe/AC and 7Co7Ni/AC, respectively after 64 hours on stream. The deactivation of the bimetallic catalysts was due to the deposition of carbonaceous materials on the surface of the catalysts resulting in reduction of catalyst activity.

Reaction kinetics was also investigated to identify the possible reaction mechanism and kinetic parameters. The best fitted model suggested the carbide mechanism as the dominant reaction mechanism in this study. The activation energies for both bimetallic catalysts; 7Co7Ni/AC and 10Co5Fe/AC are 79 and 75 kJ/mole, respectively. The lower activation energy and increased reaction rate constant k for the bimetallic catalyst 10Co5Fe/AC suggested a faster reaction was achieved on its surface in comparison to bimetallic catalyst 7Co7Ni/AC.

In conclusion, the employment of bimetallic Co-Ni and Co-Fe catalysts supported by AC in Fischer-Tropsch reaction has significantly enhanced the catalytic activity and improved gasoline selectivity. The AC generated from agricultural waste has a potential to be used as a catalyst support for the FTS reaction.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS MANGKIN DWILOGAM DISOKONG PADA KARBON TERAKTIF UNTUK TINDAKBALAS FISCHER-TROPSCH

Oleh

AHMED SHAMIL ABDULRAHMAN

Januari 2019

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Sintesis Fischer-Tropsch (FTS) merupakan satu proses untuk menukarkan campuran H_2 dan CO gas sintesis yang terhasil daripada penggasan biomas kepada bahan api bersih berkualiti tinggi dengan kandungan sulfur di bawah kewujudan pemangkin logam. Adalah dipercayai bahawa penggabungan dua logam aktif FT dengan luas permukaan tinggi dan substrak interaksi sokongan logam lemah seperti AC akan meningkatkan aktiviti pemangkin dan memperbaiki kepilihan pecahan gasolin.

Dalam kajian ini, tindakbalas FT diselidiki dalam reaktor lapisan tetap tiub pada dua kumpulan tersedia Co-Fe dan Co-Ni pemangkin yang disokong oleh AC. Pemangkin yang disintesis oleh kaedah pengisitepuan basah dan dicirikan menggunakan analisis beralatan atasan untuk morfologi dan sifat fizikal pemangkin. Penggabungan komponen logam kedua ke dalam pemangkin telah banyak mengubah sifat pemangkin dwilogam yang membawa kepada peningkatan aktiviti pemangkin dalam reaksi FT.

Kepilihan gasolin maksimum daripada 63% dan 69% telah dicapai pada pemangkin dwilogam terbaik iaitu 10Co5Fe/AC dan 7Co7Ni/AC, masing-masing. Peningkatan suhu daripada 220 °C hingga 300 °C meningkatkan kepilihan gasolin daripada 63% kepada 88% dan 69% kepada 92%. Di samping itu, penukaran karbon monoksida (CO) meningkat daripada 46% kepada 72% dan 43% kepada 65% pada kedua-dua pemangkin dwilogam 10Co5Fe/AC dan 7Co7Ni/AC, masing-masing . Sebaliknya, peningkatan tekanan tindakbalas daripada 1 bar kepada 9 bar menurunkan kepilihan gasolin dari 88% kepada 22% dan 92% kepada 36% namun peningkatan penukaran CO daripada 72% hingga 97% dan 65% kepada 84% pada kedua-dua pemangkin dwilogam 10Co5Fe/AC dan 7Co7Ni/AC. Keadaan tindakbalas optimum telah dipertimbangkan berdasarkan kepilihan maksimum gasolin dengan suhu tindakbalas 300 °C dan tekanan tindakbalas 1 bar. Pengurangan dalam kepilihan gasolin sebanyak

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42% dan 27% serta pengurangan penukaran CO sebanyak 56% dan 34% telah dilihat pada kedua-dua pemangkin dwilogam 10Co5Fe/AC dan 7Co7Ni/AC, masing-masing selepas 64 jam di aliran. Penyahaktifan pemangkin dwilogam adalah disebabkan oleh pengendapan bahan berkarbon di permukaan pemangkin yang mengakibatkan pengurangan activiti pemangkin.

Tindakbalas kinetik juga disiasat untuk mengenal pasti mekanisme tindakbalas munasabah dan parameter kinetik. Model suaian terbaik mencadangkan mekanisme karbida sebagai mekanisme tindakbalas dominan dalam kajian ini. Tenaga pengaktifan untuk kedua-dua pemangkin dwilogam; 7Co7Ni/AC dan 10Co5Fe/AC adalah 79 dan 75 kJ/mol, masing-masing. Tenaga pengaktifan yang lebih rendah dan peningkatan kadar tindakbalas pemalar k untuk pemangkin dwilogam 10Co5Fe/AC menunjukkan tindakbalas yang lebih cepat dicapai pada permukaan berbanding pemangkin dwilogam 7Co7Ni/AC.

Kesimpulannya, penggunaan pemangkin dwilogam Co-Ni dan Co-Fe yang disokong oleh AC dalam tindakbalas Fischer-Tropsh telah meningkatkan aktiviti pemangkin dan memperbaiki kepilihan gasolin. AC yang dihasilkan daripada sisa pertanian berpotenti untuk digunakan sebagai sokongan pemangkin untuk tindakbalas FTS.

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LIST OF ABBREVIATIONS

FTS	Fischer-Tropsch Synthesis
AC	Activated Carbon
BTL	Biomass To Liquid
GTL	Gas To Liquid
CTL	Coal To Liquid
WGS	Water-Gas Shift
TOS	Time On Stream
LTFT	Low Temperature Fischer-Tropsch
HTFT	High Temperature Fischer-Tropsch
CFB	Circulated Fluidized Bed
FFB	Fixed Fluidized Bed
BET	Brunauer-Emmett-Teller
EDX	Energy-Dispersive X-ray Spectroscope
FT-IR	Fourier Transform Infrared
GC	Gas Chromatograph
TPR-H_2	Hydrogen-temperature Programmed Reduction
FESEM	Field Emission Scanning Electron Microscope
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction
MARR	Mean Absolute Relative Residual
LHHW	Langmuir–Hinshelwood–Hougen– Watson

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CHAPTER 1

INTRODUCTION

1.1 Overview

Fuels derived from crude oil have dominated for a long time as a source of transport fuels. Researches have revealed that crude oil is a limited and non-renewable resource, and in the last years, there has been a big concern about the depletion of the global crude oil reserves (Owen et al., 2010). The focus recently has been shifted from the conventional fuels to alternative sources of energy, due to the high oil prices, increasing environmental concerns and depletion of fossil fuel reserves. Biomass, however, is a less predominant source, which is considered as a source of clean energy. Currently, biomass has been recognized as one of the major replacement to the decreasing conventional energy resources (Demirbas, 2007). Biomass derived fuels are identified as a great importance mostly due to their very low sulfur emissions (Özçimen and Karaosmanoğlu 2004). Furthermore, their abilities to have low lifecycle CO_2 emissions, when they are sustainably grown and consumed (Hamelinck et al., 2004). It is believed that biomass can supply one third of the world's energy demand, which is led to the improvement of technology for utilizing and employing the biomass energy (Boerrigter et al., 2003). There are several ways for the production of biofuels, which can be conducted by a number of thermochemical means:

(1) Direct combustion to produce heat, (2) Biomass gasification to produce syngas, followed by catalytic conversion to synthesize liquid fuels through Fischer-Tropsch synthesis (FTS), which is identified as biomass to liquid process (BTL) and (3) Biomass pyrolysis/liquefaction to produce liquid fuels (Hamelinck et al., 2004). The different thermochemical pathways to convert biomass to energy are shown in Figure 1.1.

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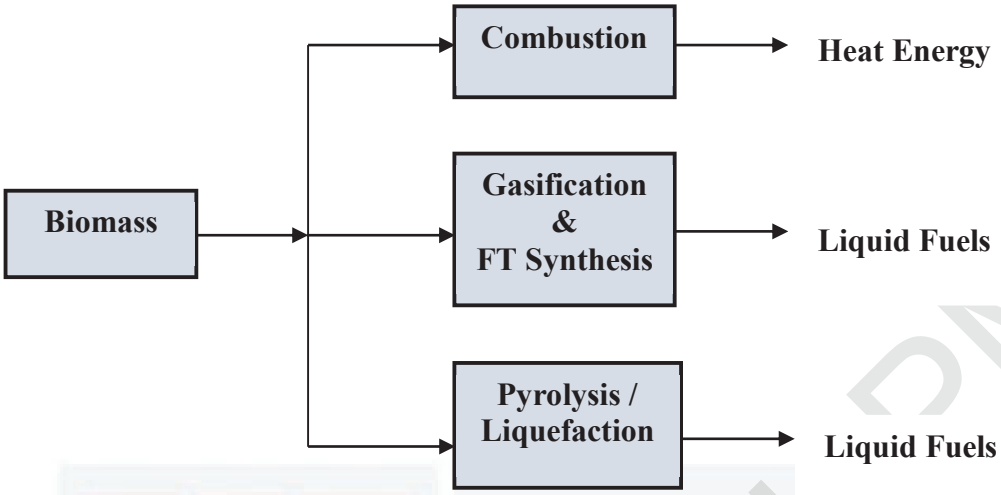

Figure 1.1 : Thermochemical pathways to convert biomass to energy sources (Damartzis and Zabaniotou, 2011)

To convert biomass into liquid fuels, the biomass has to experience several stages; firstly, biomass is converted to syngas through gasification. Gasification is the process where the organic raw material is converted to gaseous mixtures of CO, CO_2, H_2 and CH_4 by reacting with the raw materials at high temperature without combustion (Damartzis and Zabaniotou, 2011). Preceding gasification, the raw feed is generally pretreated via grinding or drying. Drying is the most critical step in the pretreatment process in order to obtain a high efficiency gasification procedure. It reduces the content of biomass moisture to less than 15 % (Hamelinck et al., 2004). Different compositions of synthesized gas are acquired by different gasification methods such as atmospheric or pressurized, direct or indirect and air blown or oxygen blown. The flow diagram for the conversion of biomass to fuels is shown in Figure 1.2. The process of gasification and the following cleaning usually requires almost 75% of the total cost of the BTL conversion process investments. Therefore, the selection of the gasifier is critically important to the process of BTL conversion. Gasification generally involves pyrolysis, char gasification and partial char combustion. Tars are also produced during pyrolysis of the solid fuel in the temperature range of 400 _ 800 °C along with CO, H_2, N_2, CH_4 and hydrocarbons. In gasification, the main target is to increase gaseous products and decrease condensable hydrocarbons, tars and char by product (Boerrigter et al., 2003; Hamelinck et al., 2004).

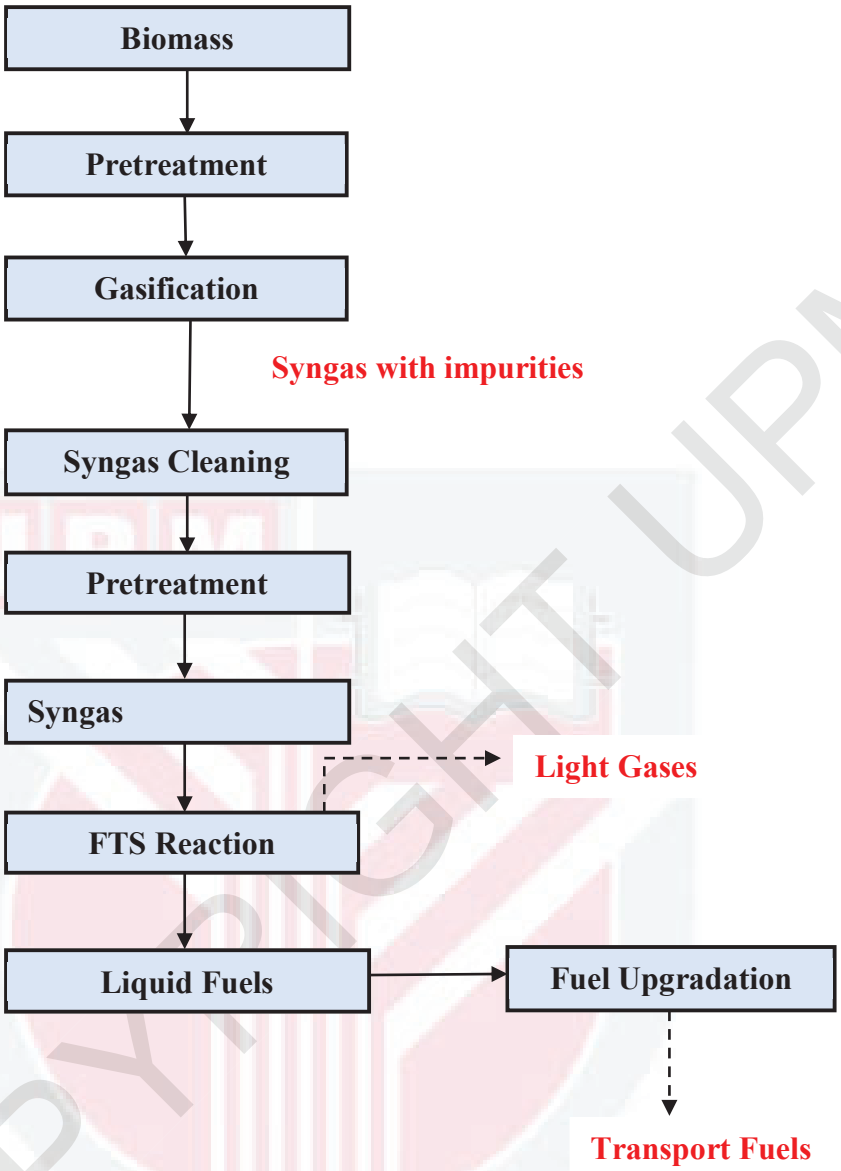

Figure 1.2 : Biomass conversion to transport fuels through FTS
(Damartzis and Zabaniotou, 2011)

Syngas obtained from the gasification process usually comprises impurities such as benzene, toluene, xylene (BTX) and other impurities such as NH_3, HCl, H_2S, HCN, dust, moisture and tars. These impurities have a major effect on the deactivation of the FT catalyst over a period of time due to catalyst poisoning (Hamelinck et al., 2004). Therefore, syngas cleaning is a very critical step in the FTS activities.

Syngas also contains large amounts of N_2, CO_2, CH_4 and low H_2/CO ratio (Damartzis and Zabaniotou, 2011; Demirbas, 2007). The H_2/CO ratio has a significant role in selecting the type of catalyst for FT reaction, and also the type of process. Co based catalysts usually need high H_2/CO ratio, while Fe based catalysts can effectively use syngas, since it possesses lower H_2/CO ratio. Steam reforming followed by water gas

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shift reaction of methane and light hydrocarbons over Ni based catalyst to produce CO_2 and H_2 is a significant procedure to improve the overall H_2/CO ratio in the syngas, and the syngas can be manipulated to reach the desired H_2/CO ratio before feeding it to the FT reactor. CO_2 can be removed from the syngas by absorption in amines.

1.2 Motivation and Problem Statement

Fischer-Tropsch synthesis (FTS) is considered as one of the most promising routes for the production of liquid fuels and chemicals from the plentiful natural gas, biomass and coal reserves. Hans Fischer and Franz Tropsch were the first who discovered the Fischer-Tropsch reaction in the year 1923 which converts a mixture of H_2 and CO into hydrocarbons and oxygenates with a wide range of chain lengths and functional groups, over a metal catalyst. Metals from group 8-10 of the periodic table, especially cobalt, iron and nickel can catalyze this reaction. Both Co and Fe based catalysts are considered as the most industrially preferred catalysts in the FT reaction, because of their high activity, selectivity, availability, lower cost and longer life period (Khodakov et al., 2007). It was reported that the incorporation of two active FTS metals enhances catalytic activity and selectivity and provides additional properties which are quite different than the one expected for monometallic catalysts. The incorporation or promotion of a second metal component into the catalyst may result in a significant modifications to either adsorption characteristics of the catalyst's surface or in some cases alter the reduction and deactivation behavior. Bimetallic catalysts possess different physicochemical properties than that of the monometallic catalysts. Previous studies have mentioned that the selectivity towards liquid hydrocarbon products was significantly increased after the incorporation of two FT active metals in a single catalyst (Bi and Dalai, 2003; Diaz et al., 2014; Ramasamy et al., 2015; Ishihara, 1987; Tavasoli et al., 2009; Wang et al., 2013).

Even though Co and Fe are more abundant than other metals that catalyze the FT reaction, these metals are limited natural resources. Therefore, their usage requires to be optimized by using a minimum amount of metals and at the same time maintaining the highest surface area. This can be executed by employing a suitable support material. Many materials were employed to support FT catalysts, such as the oxides of titanium, aluminum and silica, but the strong interaction between those supports and FT active catalysts created stable and complicated compounds which are difficult to be reduced under moderate reduction temperatures, resulted in a decrease in the reducibility of the catalysts and thus affecting their activity and selectivity greatly due to minimum number of active sites (Jacobs et al., 2002; Mogorosi et al., 2012; Yang et al., 2005). Carbon materials have emerged lately as a potential promising support for FT catalysts due to their unique properties (Antolini, 2009). Much researches on the usage of carbon materials as supports were performed on carbon nanotubes, carbon nanofibers and carbon spheres (Bahome et al., 2005, 2007; Bezemer et al., 2006; Diaz et al., 2014; Trépanier et al., 2009; Wang et al., 2013; Xiong et al., 2013), with few studies focusing on other shaped carbon materials such as activated carbon (AC). Although, many similarities are expected when AC is used as a support instead of other_carbon structures, AC is a cheaper, purer material, easy to prepare with non-catalytic synthesis methods, possess high surface area, low metal-support interaction

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and selective to gasoline as mentioned earlier in the literature (Yunxia Yang et al., 2011).

The absence of reports describing the synergistic effect between the most preferred metals in FTS such as Co-Ni and Co-Fe bimetallic catalysts supported by activated carbon in FT reaction; as well as the contradictions of the available reports about which combination of Co-Ni and Co-Fe is the most active and selective bimetallic catalyst in FTS in terms of liquid hydrocarbon production, were behind the motivation to prepare those novel catalysts and conduct this study. As a result, the influence of each metal loading in case of mono and bimetallic catalysts as well as, the influence of the applied reaction conditions on the catalytic activity and product distribution were examined and studied.

1.3 Research Aim and Objectives

The aim of this study is to synthesize active FT catalysts; consist of high surface area, low metal-support interaction and great mechanical stability activated carbon as the substrate material to support FT active metals such as cobalt, iron and nickel in both mono and bimetallic form. The synthesized catalysts are then tested in Fischer-Tropsch reaction for enhanced synthesis of gasoline fraction. To achieve this goal, three objectives should be accomplished:

1. To develop high surface area AC supported bimetallic catalysts with physical and thermal properties investigation using high-end instrumentation.
2. To assess the performance of the developed catalysts in Fischer-Tropsch reaction utilizing a fixed bed reactor at various metal loading and reaction conditions for both high gasoline selectivity and enhanced CO conversion.
3. To predict the reaction mechanism and evaluate the kinetic parameters by evaluating several kinetic models derived from different FT mechanisms.

1.4 Scope of Research

This thesis reported the synthesis of highly active FT catalysts and the great effect of incorporating high surface area and low metal-support interaction substrate such as activated carbon with Co-Ni and Co-Fe bimetallic catalysts to synthesize high selectivity gasoline fuel. The synergistic effect of two active metals supported on AC has brought additional properties to the catalyst that helped in improving the catalytic activity of the catalysts. Manipulating metal loading ratios as well as operating conditions have significantly altered gasoline fraction selectivity and CO conversion. Kinetic parameters and the potential reaction mechanism were also predicted by evaluating several kinetic models based on different FT reaction mechanisms, in order to provide better understanding about the current reaction's nature. The flow process of the present work is illustrated in Figure 1.3. The arrows represent the direction followed in order to achieve the objectives.

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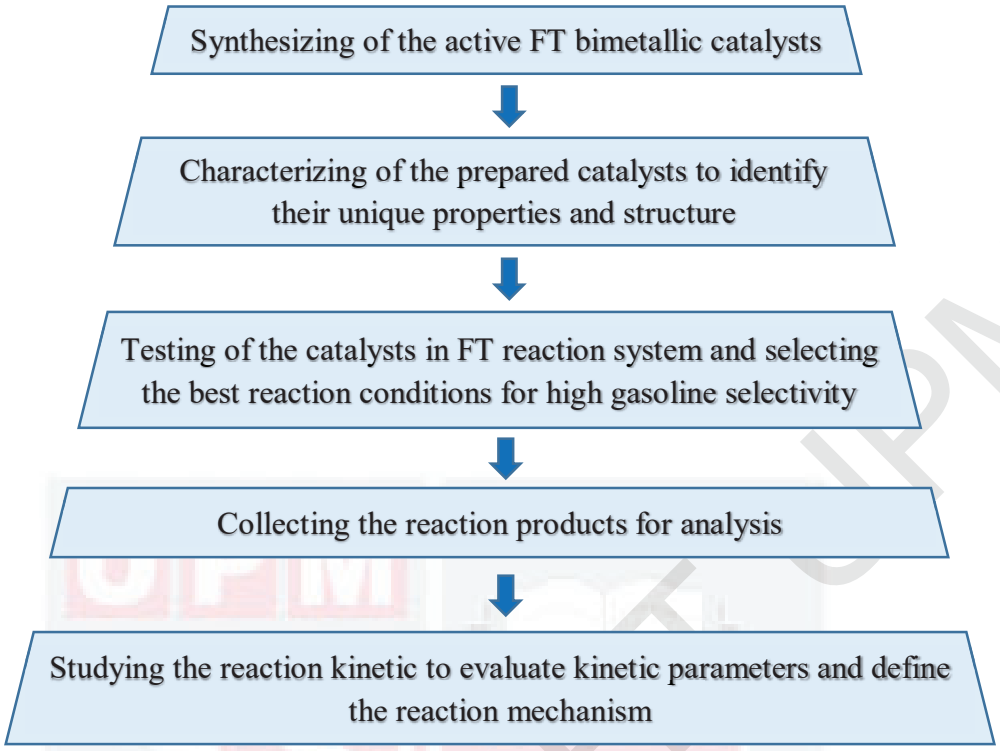

Figure 1.3 : Scope of research

1.5 Thesis Layout

The thesis is structured into six chapters; which are summarized as follows:

Chapter 1 provides general introduction of the research area, and identifies the different routes to produce biofuels. Furthermore, the conversion of synthesized gas to liquid fuels was also displayed as it is the motivation behind this study. It also introduces the problem statement, research aim and objectives, scope of research and thesis layout.

Chapter 2 provides a thorough review of Fischer-Tropsch reaction including the history of FT reaction, the suggested chemistry and mechanisms, product distribution, the catalysts and reaction systems employed, as well as the main reports and studies that were conducted in this field.

Chapter 3 presents the methodology and experimental work by discussing the synthesis of the supported catalysts, the different characterization methods that have been investigated and the employed reaction system to test the prepared FT catalysts.

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Chapter 4 discusses the results and major findings from the different characterizing methods and the effect of those examined physical and thermal properties on the performance of the prepared catalysts.

Chapter 5 discusses the catalyst performance in FT reaction, in terms of product distribution and CO conversion. Furthermore, the chapter also investigates the effect of metal loading ratio and operational conditions on the gasoline selectivity and deactivation of the catalysts.

Chapter 6 predicts the potential reaction mechanism and kinetic parameters, by evaluating several mathematical models based on different FT mechanism theories.

Chapter 7 provides a summary of the entire thesis and conclusion takes place. Followed by further ideas and suggestions for potential future work.

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