Development of Carbon Supported Iron Catalyst for Liquid Fuel Production from Coal/Biomass Derived Syngas

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Session 2015-17

Supervised by
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THESIS ACCEPTANCE CERTIFICATE

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Dedication

I dedicate this work to my parents and family for their love, motivation and inspiration

Abstract

As the resources of crude oils are depleted and the environmental problems are increased due to the green houses gases emissions which are being damage the ozone layer. The worldwide researchers have concern to produce the alternative process for the production of chemicals and hydrocarbons form coal and biomass. The Fischer- Tropsch synthesis process provides the clean production of hydrocarbons from the mixture of hydrogen and carbon. All the production of hydrocarbons is free from sulfur content. Different kind of promoters and binders are commonly used in iron based catalyst in order to increase the selectivity of hydrocarbons. Potassium is used as a chemical promoter and silica and alumina are used as a structural promoter. Potassium has a variety of advantage; they increase the amount of alkenes in hydrocarbons production and suppress the formation of methane. There are several Fischer Tropsch synthesis plants which are currently producing liquid hydrocarbons all over the world to meet the human needs with a different proposed mechanism. Iron based catalyst is largely used due to his water gas shift activity and low cost and received a immense attention of researchers. Now a day carbon supported iron based catalyst are highly preferred due to his low cost and better C5+ selectivity of desire hydrocarbons. So first of all activated carbon are prepared by wet impregnation method to develop a carbon supported iron based catalyst. Different types of characterization technique are carried out to find out the properties such like Scanning electron microscopy is a technique which can be used to find out the structural properties of the crystal. X-ray diffraction (XRD) is the technique to find out the phase of an unknown crystalline material and also the information about the crystal shape and size. EDS was used for the elemental analysis and TGA gives the information about the thermal degradation of the material. Then prepared catalyst is run into Fischer Tropsch synthesis reactor to find out the production of gasoline. The carbon supported iron catalyst with potassium promoter increase the catalyst activity and selectivity toward the desire hydrocarbons. The highest quantity of C_8 is much higher than the other hydrocarbons present in the product sample. The total percentage of different hydrocarbons in the mixture is (C_5-C_7) is 9% and (C_8-C_{23}) is 91%. Different types of promoter can also be used in order to increase the C_{5+} selectivity.

Key words: Wet impregnation Method; Fischer Tropsch Synthesis; Carbon Supported Iron Catalyst; Potassium Promoter; Water Gas Shift;

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List of Abbreviation

GHG	Green House Gasses
CTL	Coal to Liquid
DCL	Direct Coal Liquefaction
ICL	Indirect Coal Liquefaction
DMF	Dimethylformamide
BLT	Biomass to Liquid Technology
GTL	Gas to Liquid Technologies
FTS	Fischer Tropsch Synthesis
BPD	Barrels per Day
FBR	Fixed Fluidized Bed Reactor
MOF	Metal Organic Framework
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
TGA	Thermo Gravimetric Analysis
GCMS	Gas Chromatography and mass spectroscopy
HTFT	High Temperature Fischer Tropsch
LTFT	Low Temperature Fischer Tropsch
PBSi	Phosphorus, Boron and Silicon

List of Publications

Muhammad Amin , Saleem Munir, Naseem Iqbal, *Synthesis and characterization of activated carbon from olive tree by* H_3PO_4 *chemical activation*, 5th International Conference on Phosphorous, Boron and Silicon PBSi-2017, 03-05 July 2017 in France (Accepted)*

Muhammad Amin, Saleem Muir, NaseemIqbal, *Development of MOF derived iron catalyst for a Fischer Tropsch synthesis*, International Conference on Recent Innovations in Science, Engineering, Technology and Management (ASAR-ICRISETM-2017), 15 July 2017 in India (Accepted)**

* Annex I
**Annex II

Chapter 1: Introduction

1.1 Introduction

A German scientist had invented the Fischer-Tropsch process in which synthesis of hydrocarbons from syngas are performed (a mixture of hydrogen and carbon monoxide). At that time different process industries such like SASOL and Shell are working on this field and they are producing a large variety of hydrocarbons in a large scale from syngas. In general Fischer Tropsch synthesis is a type of catalytic reaction and two catalysts "iron and cobalt" are mainly used as an active and selective catalyst for FT process. Iron based catalyst is largely used due to his water gas shift activity and low cost and received a immense attention of researchers [1].The Fischer- Tropsch synthesis process provides the clean production of hydrocarbons from the mixture of hydrogen and carbon. All the production of hydrocarbons is free from sulfur content that is very big advantage. Very common sources of syngas are classified from natural gas and as well as from coal. That FT process can be used to produce a hydrocarbon chain C_5-C_{11} (gasoline) and C_{12}-C_{18} (Diesel) and have a ability to produce a value able transportation fuel [**2**].The Fischer-Tropsch synthesis reaction is

$$CO + (1+n/2)\ H_2 \rightarrow CH_n + H_2O$$

Where 'n' is present the average ratio (H/CO) of hydrocarbons which are being produced. Different kind of promoters and binders are commonly used in iron based catalyst in order to increase the selectivity of hydrocarbons. Potassium is used as a chemical promoter and silica and alumina are used as a structural promoter. Potassium has a variety of advantage; they increase the amount of alkenes in hydrocarbons production and suppress the formation of methane [3].Iron based catalysts are classified into a supported and bulk catalyst both one is prepared by wet impregnation method. In a supported iron catalyst requires an addition of metal- support in order to prevent the particle agglomeration. They have also ability to exhibit a higher mechanical strength as compared to bulk iron catalyst [4].

As the resources of crude oil are depleted and the environmental problems are increased such as the green houses gases emissions damage the ozone layer then the worldwide researchers have concern to produce the alternative process for the production of chemicals. Sintering provides the fast deactivation in iron based catalyst. Carbon deposition and phase change have a proven challenging in cobalt based catalyst [5].

1.2 Background of Fischer Tropsch Synthesis

More than seventy years has been done in a Fischer–Tropsch (FT) synthesis process. Today it provides a clean transportation fuels as well as different industrial chemicals. Franz Fischer was well aware of industrial organic chemistry when the gases of CO and H_2 enter into the reactor with the presence of heterogeneous catalyst and that vision takes might importance when the reserves of oil and gas are being consumed in very short time and the demand of hydrocarbons are increased [6].In1902, when Sabatier and Sendersen report the formation of methane from CO and hydrogen by using a Ni and Co based catalysts. After few years in 1908, Orlov finds the ethene with the use of Ni-pd catalysts. 1913 BASF, and in 1924 Fischer and Tropsch report about the preparation of hydrocarbons over an Fe catalyst. In 1936 commercialization of FT process are started and produced 200,000 t/year capacities. In 1955, Sasol I starts the production with the combination of fixed and fluid bed reactors. In 1994, Shell starts operating plant in Malaysia with SMDS process and now with the passage of time several large GTL processes are working and some of these are under construction. During the World war II, the Fischer Tropsch synthesis has become more important in order to satisfy the demand for fuel. Fe, Co and Ru are the most widely use catalysts in World War II [7].1920s as the demand of liquids products in automobiles, airplanes and petroleum powered ships are increased then researcher's starts the thinking for production of liquid fuels from wood and cool in order to meet the human needs. When Industrialized nations such like Germany, Britain, Canada, France, Japan, Italy, and other nations having little or no more domestic petroleum resources to continued to import petroleum then they synthesized the petroleum from the coal resources [8].

1.3 Industrialization of the Fischer Tropsch Process

1.3.1 Sasol

Sasol is a plant located in a South Africa and using a synfuel technology for the production of liquids products. Mossgas complex has the world's largest synthetic fuel project that was commissioned in 1993 at Mossel Bay in South Africa with a production of 25 000 barrels per day. Sasol has modified its Arge reactor in order to increase the higher molecular weight hydrocarbons and also operates slurry phase distillate process that is the recent most reactors working in Sasol. Slurry phase distillate process shows more olefinic and straight chain paraffin’s than the other types of reactors. They are working on cobalt and iron based catalyst by using Sasol Advanced Synthol reactor to produce the light olefins and gasoline. Sasol Slurry Phase Distillate plant is converts 100 MMSCFD of natural gas into 10, 000 barrels a day of liquid fuels with a capital cost of about US$250 million.

1.3.2 Statoil

Statoil plant located in Norway’s, and they are working on catalyst development as well as reactor processes (three –phase slurry reactor) to produce liquid products with the use of their natural gas. The main challenged they are facing in the catalyst performance in order to extract the liquid product.

1.3.3 Shell

Shell has built a plant in Bintulu a city of Malaysia for a capacity of 12 000 bbl/day in 1993 and they are producing a highly paraffinic which are free of nitrogen and sulfur. Within the duration of 10 years Shell has investing more than US$6 billion in a four plants for the production of liquid products.

1.3.4 Exxon

Exxon has used natural gas as feedstock for the developed a commercial FT. Exxon are working on fluid bed , synthesis gas generation by catalytic partial oxidation, slurry phase F-T synthesis and fixed bed product upgrade by hydro-isomerisation.

1.3.5 Syntroleum

The Syntroleum Corporation is a FT process plant located in USA which is being producing a diesel with the using of natural gas as a feedstock. They are using air-based auto thermal reforming process in order to eliminate the cost of air separation unit. The production capacity of synthetic crude is $20 per bbl.

1.3.6 Rentech

With the use of precipitated iron catalyst, Rentech a plant located in USA are converting the gases by straight chain hydrocarbons with the help of molten wax slurry reactor.

1.3.7 Methanex

Methanex plant located in a New Zealand and working on two different technologies (i) methanol-based routes to gasoline and (ii) Mobil's methanol-to-gasoline (MTG). These processes are based on the fluid bed reactor with a catalyst of ZSM-5 zeolite.

1.3.8 Other production sources

A Mossgas plant present in a South Africa and his capacity of production oil is around 1000 bpd. In recent years Qatar Petroleum starts their production 34,000 bpd in a Oryx city of Qatar. Exxan Mobile and Qatar Petroleum has lot of huge contribution toward the oil production from coal. The plant is located in north east of Doha and his production is 154,000. The series of plant are located in worldwide and complete detail is mention in a given below table.

Table 1 Currently operational Fischer Tropsch plants in World wide

Year	Plant/ Company	Production Level (bpd)	Country	City
1944	SHL	14,000	Germany	Ruhland-Schwarzheide
1955	Sasol-I	5600-8000	South Africa	Sasolburg
1980	Sasol II	$124 *10^3$	South Africa	Secunda
1983	Sasol III	$154*10^3$	South Africa	Secund
1991	PetroSA	$22.5*10^3$	South Africa	Mossel Bay
1993	Bintulu GTL	14,700	Malaysia	Bintulu
1952	JSC Novocherkassk	50,000 t/y	Russia	Rostov
1985	ExxonMobil	14,500	New Zealand	New Plymouth
2002	Mossgas	1000	South Africa	Mossel-Bay
2004	SLH	400	USA	Ponca City
2006-2012	Qatar Petroleum/Sasol	$34*10^3$	Qatar	Oryx
2006	Qatar Petroleum/Shell	$140*10^3$	Qatar	Ras Laffan
2011	Exxan Mobile and Qatar Petroleum	154,000	Qatar	North East Doha

Reference: Gas to Liquids, Historical Development and Future Prospects, Olga Glebova, Nov 2013, The Oxford institute for Energy studies.

1.4 Fischer Tropsch Chemistry

The reaction take place in Fischer Tropsch synthesis is classified into main reactions, side reactions and catalyst modification reactions.

1.4.1 Main Reactions

Paraffin formation:

$$(2n + 1)H_2 + nCO \rightarrow nH_2O + C_nH_{2n} + 2 \qquad (1.1)$$

Olefin formation

$$2nH_2 + nCO \rightarrow nH_2O + C_nH_{2n} \qquad (1.2)$$

Water-gas shift (WGS) reaction

$$H_2O + CO \leftrightarrow H_2 + CO_2 \qquad (1.3)$$

1.4.2 Side Reactions

Alcohol production

$$2nH_2 + nCO \rightarrow (n - 1)H_2O + C_nH_{2n} + OH \qquad (1.4)$$

Boudouard reaction

$$2CO \rightarrow C + CO_2 \qquad (1.5)$$

1.4.3 Catalyst Modifications

Catalyst oxidation/ reduction

a. $yCO + MxOy \leftrightarrow xM + yCO_2$ (1.6)

b. $yH_2 + MxOy \leftrightarrow xM + yH_2O$ (1.7)

Bulk carbide formation

$xM + yC \leftrightarrow MxCy$ (1.8)

Where ‘n’ is the carbon number which depending on a number of factors, primarily the H2/CO ratio in the syngas and the type of catalyst employed.

1.5 Fischer Tropsch synthesis Mechanism

Fischer Tropsch synthesis process steps can be classified into six step which are the following, reactant adsorption, chain initiation, chain growth, chain termination, product desorption and re-adsorption and further reaction. Reaction path in Fischer Tropsch synthesis are clarify with the help of surface carbide mechanism, enol mechanism, CO insertion mechanism and alkenyl mechanism.

1.5.1 Surface carbide mechanism

Surface carbide mechanism was developed by Craxford and Rideal, in which the carbon monoxide is adsorbed on the surface and dissociates to forming water in the presence of hydrogen. The carbon is hydrogenated to form chemisorbed CH_2 which are ologimerizes to produce higher carbon number hydrocarbons.

$Co + CO \rightarrow Co–CO$ (9)

$Co–CO + H_2 \rightarrow Co–C + H_2O$ (10)

$$\text{Co–C} + H_2 \rightarrow \text{Co–CH}_2 \rightarrow \rightarrow \text{higher hydrocarbons} \quad (11)$$

1.5.2 Surface Enol Mechanism

In this mechanism, chain growth with the un-dissociative chemisorption of Carbon monoxide (CO) which then reacts with adsorbed hydrogen (H_2) to generate enolic (HCOH) units. The structure of product then increased by a combination of surface-polymerization-condensation and elimination of water (H_2O).

1.5.3 CO Insertion Mechanism

CO-Insertion mechanism can be classified into few steps (i) adsorption of reactant and reactant consist of CO and H_2 . (ii) chain initiation (iii) chain propagation and finally chain termination step. In the below figure CO-Insertion mechanism is listed.

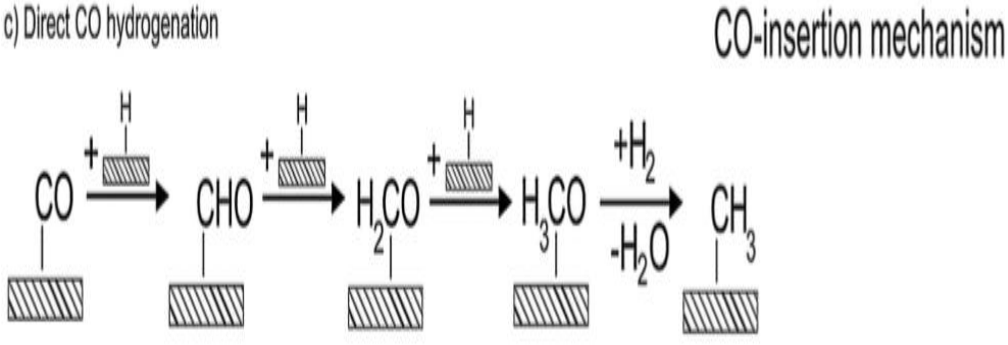

Figure 1: CO-Insertion mechanism

1.5.4 Alkenyl Mechanism

The alkenyl mechanism proposed by Maitlis and co-workers. The mechanism suggests that polymer-chain carriers are surface-alkenyl rather than alkyl-species. The CH_2 surface-species is considered as the chain propagation monomer. The surface vinyl-species ($–CH=CH_2$), which is a chain starter, is generated by the reaction of a surface-methyne ($\equiv CH$) and surface-methylene ($=CH_2$) species. Chain growth occurs by the coupling of a sp2 (alkenyl) carbon with a sp3 (methylene) carbon to form an allyl species ($–CH_2CH=CH_2$).

It has been shown in the literature [38] that the coupling of sp2 with sp3 carbons in metal complexes is a lower energy process than a Csp3 + Csp3 coupling reaction. The surface allyl species then isomerizes to the more reactive propenyl species ($–CH=CHCH_3$). Termination occurs by the reaction between surface hydrogen and the surface alkenyl species yielding predominantly α-olefins. This mechanism was tested by adding ethene-$13C_2$ probes during FTS. Advantages of this mechanism include explaining; the formation of branched products (for example by allyl isomerization), the low amount of C_2 products, and the release of 1-alkenes as primary products (by a favorable hydrogenation reaction).

However this mechanism is inadequate when explaining the formation of n-paraffin and the formation of oxygenates. The key step in the mechanism proposed by Maitlis et al. is the allyl–vinyl isomerization, yet no experimental evidence for such a facile isomerization has been given.

Summary

As the resources of crude oil are depleted and the environmental problems are increased such as the green houses gases emissions damage the ozone layer then the worldwide researchers have concern to produce the alternative process for the production of chemicals. The Fischer- Tropsch synthesis process provides the clean production of hydrocarbons from the mixture of hydrogen and carbon. Iron based catalyst is largely used due to his water gas shift activity and low cost and received a immense attention of researchers. Different kind of promoters and binders are commonly used in iron based catalyst in order to increase the selectivity of hydrocarbons. Potassium is used as a chemical promoter and silica and alumina are used as a structural promoter. Potassium has a variety of advantage; they increase the number of alkenes in hydrocarbons production and suppress the formation of methane. There are several Fischer Tropsch synthesis plants which are currently producing liquid hydrocarbons all over the world to meet the human needs with a different proposed mechanism.

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Chapter 2: Literature Review

2.1 Fischer-Tropsch Reactors

Low temperature Fischer Tropsch reactors are classified into tubular fixed bed, micro channel and slurry bubble column reactors and their different characteristics and conversion per path are shown in a table below. Micro channel reactors show a superior productivity per reactor volume other than reactors.

2.1.1Fluidized Bed Reactor

In a fluidized bed reactor a high velocity of fluid flows through the solid particles in order to causing the towler (fluidization). These types of reactor are operated at high temperature at the range of 350℃, 25 bar pressure and the quality of heat removal is high.

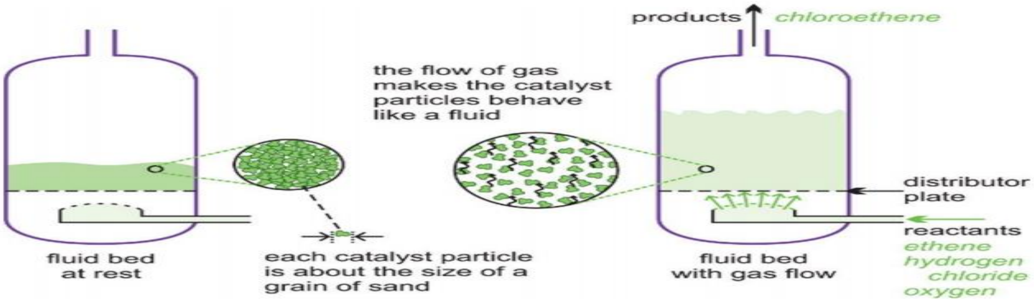


Figure 2: Fluidized Bed Reactor

Table 2: Properties for different reactor types for Low-Temperature Fischer Tropsch synthesis

Reactor	Conversion per path (%)	Capacity per reactor (bbl/day)	Characteristics
Tubular fixed-bed	30-35	≤6000	≤30,000 tubes with catalyst pellet or extrudates
Slurry bubble column	55-65	≤25,000	Internal heat exchanger and optional product filter
Micro-Channel	65-75	≤1000	Metal block with < 2nm diameter channels

2.1.2 Fixed-bed reactor

Now a day's design of fixed bed reactors is based on a multi tubes heat exchangers due to control of heat effectively. Their designing contains shells (evaporating water) and tubes (catalyst in the form of pellets is loaded into tubes). Main thing in a fixed bed reactor is that to avoid generating a hot spot because they cause sintering during the reaction. To remove the deactivation the following changing in tube diameter and size of catalyst are change is performed. Deactivation problem in a fixed bed reactor are solved be varying a partial pressure of reactant as well as a product and also size of catalyst within a tube length. Overall temperature in fixed bed reactor is slower than slurry bed reactor because the average composition of gases is richer than hydrogen. Within a reactor shell thousand ten of tubes are incorporated which can optimized the production and scale up the process and saving the timing. Loading and unloading of the tubes creates a problem in the catalyst process which are generally is fouling and these must be controlled during the reaction. The syngas entered above into the reactor and product are collected at the bottom of the reactor with a multiple tube are shown in below figure.

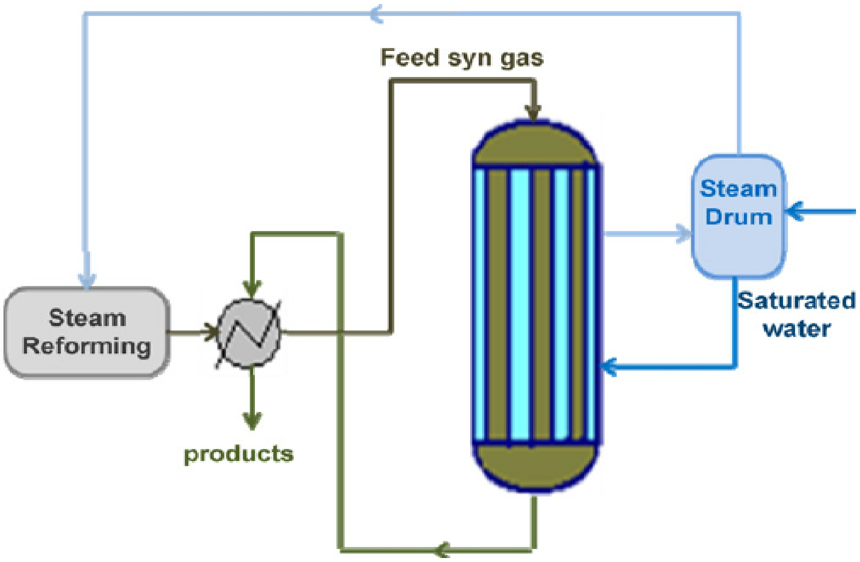


Figure 3: Schematic diagram of a fixed-bed single stage Fischer–Tropsch synthesis reactor [2]

2.1.3Slurry bubble-column reactor (SBCR)

In slurry bubble column reactor catalyst particles are suspended and the reactant gases are bubbled through the column. The concentration of the solid particles from bottom to top is diminishing which are depending on the density of the catalyst particle, superficial gas velocity and their catalyst diameter. Liquid products are collected from the bottom and gases products are from top of the process. Two main factors which are controlled one are the overheating and other is settling of the catalyst both causes the deactivation. Slurry bubble column reactor have simple in construction, high heat transfer coefficient and high space time yield. In order to achieve high selectivity of hydrocarbons in slurry bubble column reactor we have to proper liquid and gas mixing and maintain the exit water concentration. The higher exit water concentration reduces the coke deposition during the process. In order to achieve a high CO conversion extensive amount of recycle syngas is required during the process.

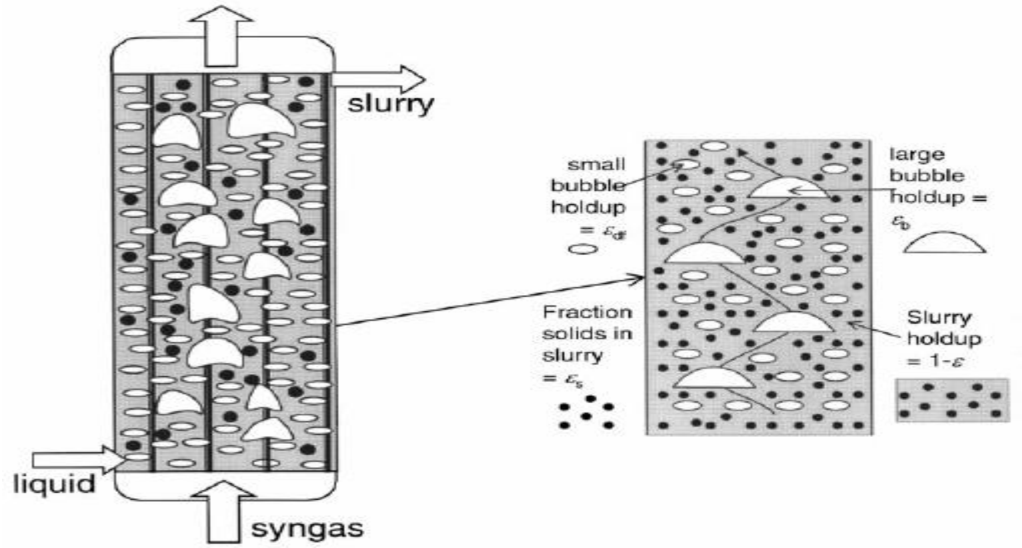


Figure 4: The bubble column slurry reactor configuration with internal cooling. On the right is a simplified description of the various phases [4]

2.1.4 Micro-channel reactor

Micro channel reactor is well known due the heat and mass transfer rates. These types of reactor are loaded with highly active and stable catalysts. Selectivity's of hydrocarbons are highly achieved with a conversion rate of 90 %.

Micro channel reactors are usually operated isothermally and pressure drop are relatively are generally low. Stability of catalyst to avoid the deactivation is done at high conversions. The operating figure of Velocys and compact GTL micro channel reactor are shown in below figure [1].

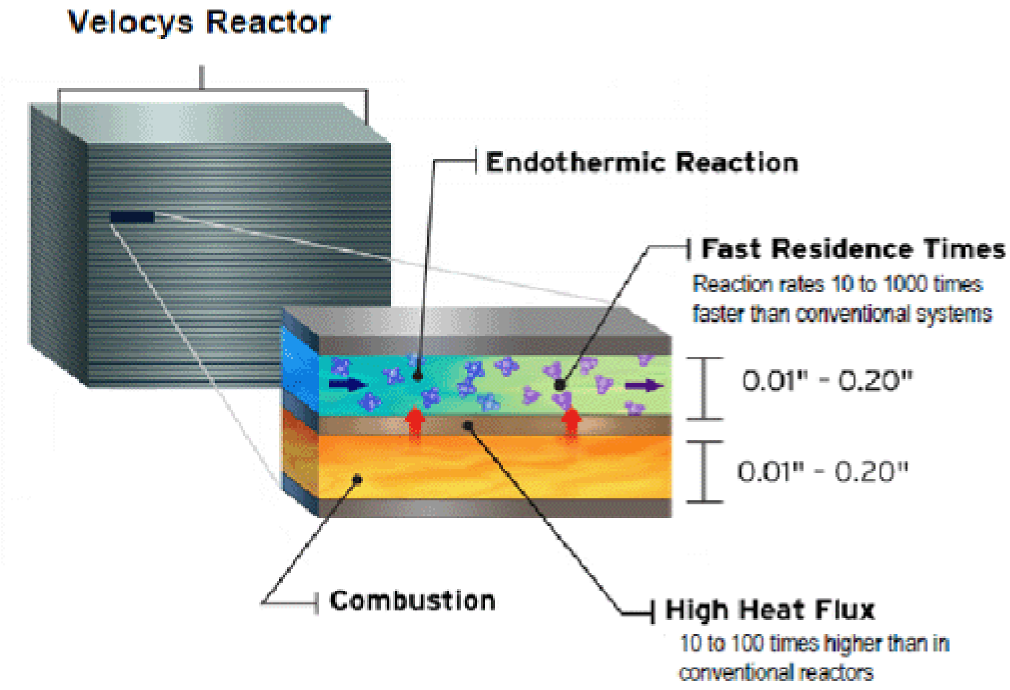


Figure 5: Velocys and compact GTL Micro channel reactor

2.2 Influence of promoters and support on precipitated Fe catalysts

For iron based catalyst alkali metals are used as a promoter which is the essential path to obtain high basicity and high surface area of specific metal. In order to decrease the activity of (Br-, Cl-, and So4) we have to decrease the highly electronegative anions. Activity of Fe-Cu-Sio_2 based catalyst are decreases in the following alkali metal activity (K>Rb>Na>Li). Rb promoters show the low activity relatively to Br due to the high wax selectivity's. Different types of supported material are added and SiO_2 shows the best results compared to other supports. If we increase the longer chain of hydrocarbons, then increase the alkali level as high as we done. Cu enhances the reducibility of the catalyst.

2.3 Types of Catalyst

2.3.1 Fused iron catalysts

Impurities level of different compounds (SiO_2, TiO_2, MgO and Al_2O_3) in iron oxide (fused iron) catalyst is significantly overlooked. In fixed bed reactor catalyst are loaded and reduction is done through hydrogen. In order to analyzed the particles through microscopic which shows that the outer skin in the form Fe_2O_3. Particle size toward the center is increased by adding the small amount of alkali silicates. Silicates itself contain a little amount of structural promoter. During the reduction process of catalyst in a fixed bed reactor creates heterogeneity of catalyst and proper redistribution of iron.

2.3.2 Co based catalysts

Some of noble metals are used as a promoter in Fischer Tropsch synthesis process and they will enhance the activity due to the reduction in lower temperature. As well as to improve the wax selectivity transition metal oxides are added. The operating condition of catalyst are varying and normally in the range of (1-10 bar). Catalytic activity is directly proportional to the concentration of Co.

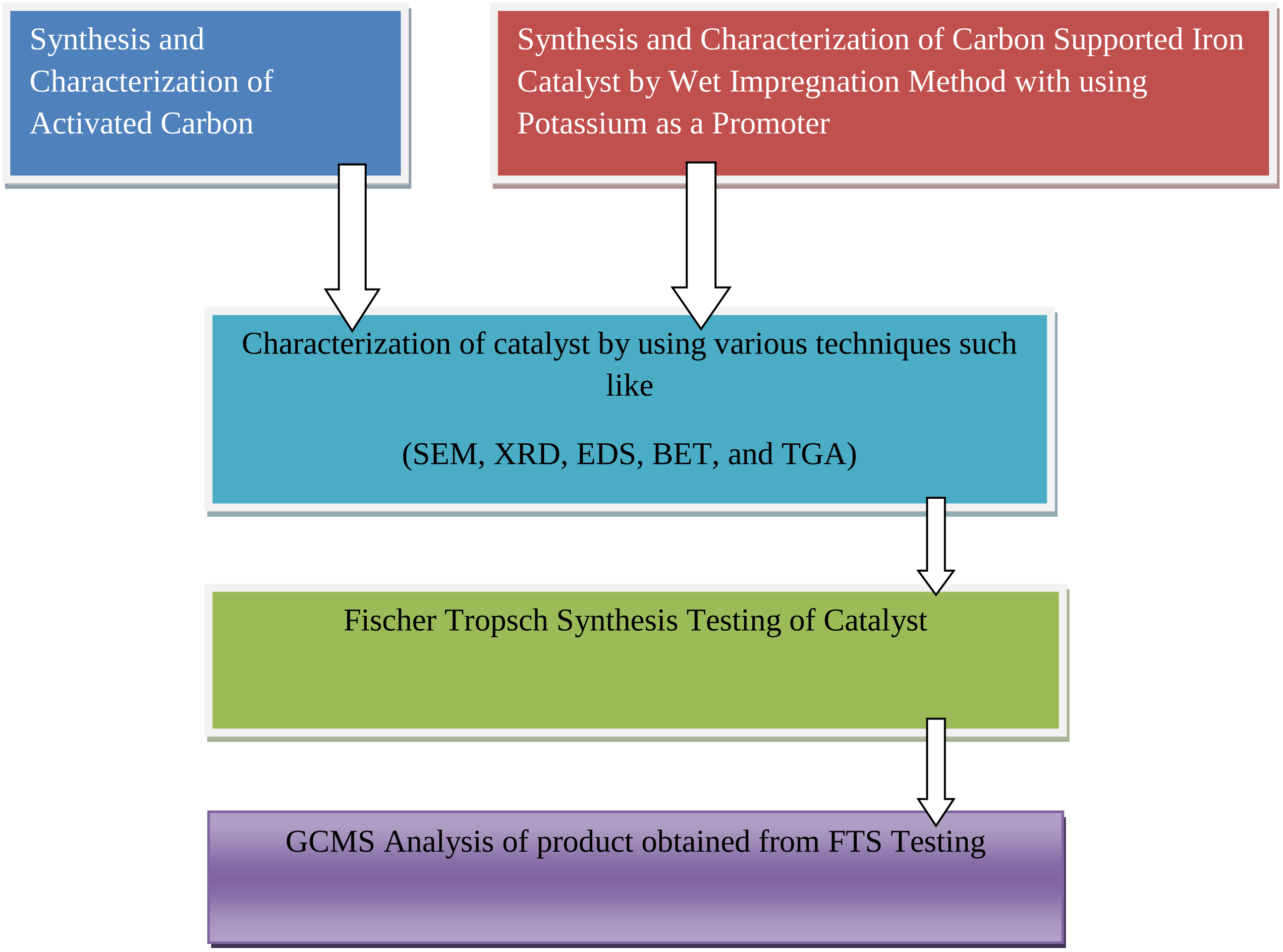
2.3.4 Ruthenium based catalysts

Conventional Fischer Tropsch catalyst behaves a better activity at lower temperature as compared to higher temperature due to the formation of methanation compounds. High pressure and low temperature are suitable to produce high molecular mass waxes. Ru also used as a supported catalyst about 5 % and they produce light hydrocarbons.

2.3.5 Alternative catalysts

Nickel based catalyst shows a good methanation and hydrogenolysis activity in Fischer Tropsch synthesis process. They show a maximum level of activity when they adsorption of CO at moderate heat.

2.4 Flow chart of Thesis



Summary

There are two main type of Fischer Tropsch synthesis process. Low temperature and high temperature Fischer Tropsch reactors are classified into tubular fixed bed, micro channel and slurry bubble column reactors, fixed bed reactors and micro channel reactors. Generally different types of catalyst are used in FT reactors which are fused iron, cobalt, ruthenium and nickel based catalyst.

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Chapter 3: Review on Characterization

For the testing of catalyst several characterization techniques like XRD, SEM, BET and TGA are used for the prepared catalyst. The principles, functions and operating basic conditions of technique are mentioned below.

3.1 X-ray powder diffraction (XRD)

A German scientist “Wilhelm Conrad Rontgen” discovered the X-rays in 1895. Channel of light waves through an ordered array of scattering method are established by PP Ewald. His theory assumed in which crystals were made of space lattice particles. In 1912 the diffraction pattern was invented. The results show that x-rays have an accurate wavelength to diffract from the projected space lattice. Always diffraction of light occurs when they scattered by a periodic array. Every diffraction peak is attributed by a parallel plane of atoms and they are recognized by Miller indices. Bragg’s law can be used to check the diffraction peak position (which is the product of inter planar spacing) [1].

$$\lambda=2d_{hkl}sinq$$

The arrangement of atoms in the crystal is determined by intensity peak of diffraction.

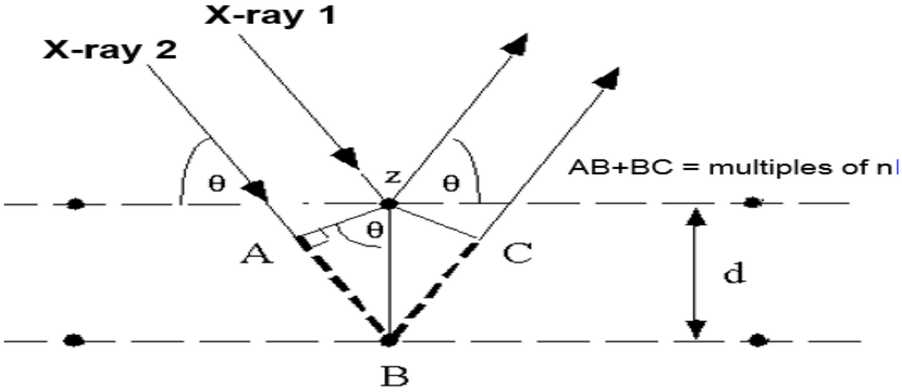


Figure 6: Pictorial demonstration of Braggs Law

3.2 Scanning Electron Microscopy

The main component of scanning electron microscopy is electronic console and the electron column. Knobs are controlled by the electronic console and switches are used to adjust the filament current, voltage, brightness and contrast. The electron column is used to produce electron beam with the help of vacuum pump. The sample image is scanned with the help of electromagnetic deflection coils. The lower portion of the column is specimen chamber and second electron detector is present above the sample stage. Free electron is produced with the help of electron gun by thermionic emission from the filament (tungsten) at temperature rang at 2700 K. The role of filament is to control the electrons which are leaving from the electron gun. Condenser lenses are inserted to converge the beam and pass through the focal point. Electron column are used to find out the aperture of sample images. These apertures reduce and exclude the extraneous electrons in the lenses. The size of the beam regulates with the help of final lens.

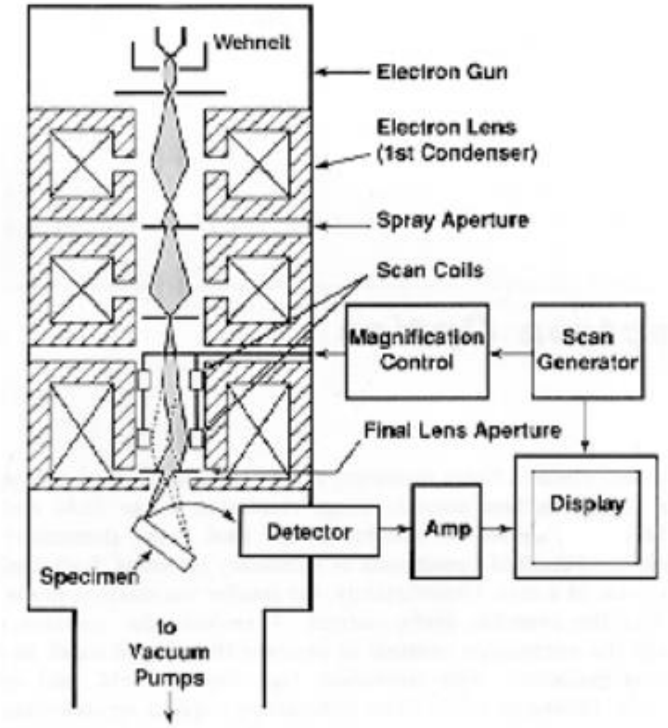


Figure 7: Scanning Electron Microscopy Instrumentation

Objective lens contains the deflection coils and image is normally formed by scanning with the rastering of electron beam. Sample chamber contains the sample stage and controls and are located at the lower portion of the column. For morphology analysis, controlled beam of electron is required which are provided with the vacuum system. A high pressure is required for the detail and good images which are normally above $5*10^{-5}$torr. The temperature of filament is around 2700 K due to the current passes through the filament **[2].**

3.3 Thermo gravimetric Analysis (TGA)

In TGA analysis, a relationship between changes in weight is related to change in temperature are measured. After that we get a weight loss curve which indicated the information about the sample composition, kinetic parameters and the thermal stability. To find out the weight loss at a specific point is determined by with the help of derivative weight loss curve. Purity level of a material and humidity level are also determined by a TGA analysis. A detail picture of thermo gravimetric analysis is shown in below figure where mass changes, adsorption and desorption of gases and phase transitions are occurring during the process **[3].**

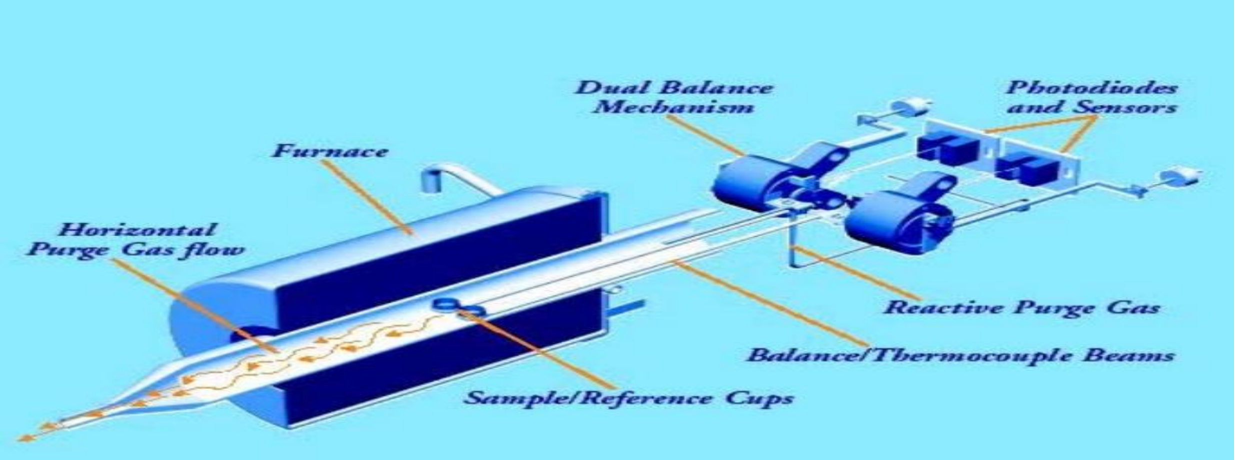


Figure 8 : Thermo Gravimetric Analysis Apparatus

3.4 Introduction to Energy Dispersive X-ray Spectrometry (EDS)

EDS are attached with the scanning electron microscopy and solid sample are bombarded with the electron of focused beam to analyze the chemical composition. All the elements can be analyses from atomic number 4 (Be) to 92 (U). X-ray microanalysis can be done when high energy electron is bombarded with the sample in an electron microscopy. To separate the x-ray with the energy level so we use energy dispersive spectrometer and that can be perceived.

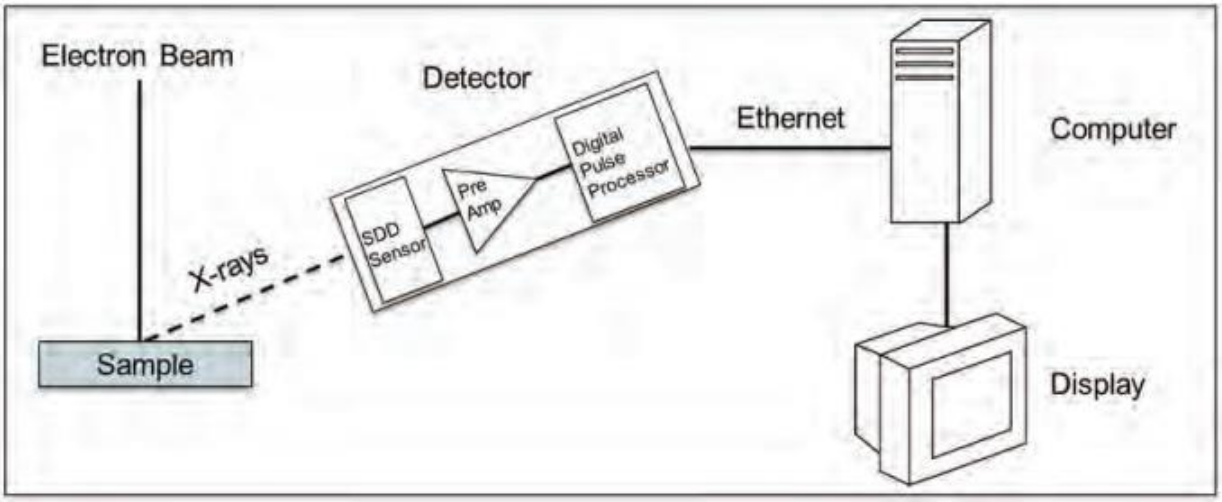


Figure 9: Introduction to Energy Dispersive X-ray Spectrometry

3.5 Brunauer-Emmett-Teller Analysis (BET)

Advancement in the Langmuir BET theory was done by a Stephen Brunauer, Paul Emmett and Edward Teller in 1938. Nitrogen gas is usually present in high purity and used to find out the surface area with the help of degassing. One of the properties of the nitrogen is that it has a strong interaction with the solid materials. The surface of sample is cooled using the liquid nitrogen instead of gases nitrogen. Operating relative pressure are less than the atmospheric pressure during the process condition. No more adsorption occurs after the saturation pressure. When the adsorption layer is occurring then sample are removed from the nitrogen atmosphere and heated. The heating is performed to remove the nitrogen to quantify the properties. Then data are displayed in the isotherm form which is relationship between gas adsorbed and the relative pressure. Possible isotherm is described below **[4].**

.

Figure 10: Brunauer-Emmett-Teller Analysis

Monolayer adsorption isotherm is called pseudo-Langmuir isotherm and the operating conditions are when relative pressure are less than 1 and c>1 in the BET equation and where ‘c’ is the BET constant. ‘c’ is related with the adsorption energy of monolayer that will be changed with solid to solid. Type II isotherm are used to analyzed the formation of monolayer. The value of constant is greater than one. Operate at low pressure gives us the micropores and high pressure capillary condensation is occurring. Type III isotherm is used for the formation of multilayer’s. There is no asymptote in the BET curve so no monolayer is formed and BET is not applicable. When capillary condensation occurs then type IV isotherm are applicable. Gases must be condensing in the pores of capillary at pressure below the saturation pressure.

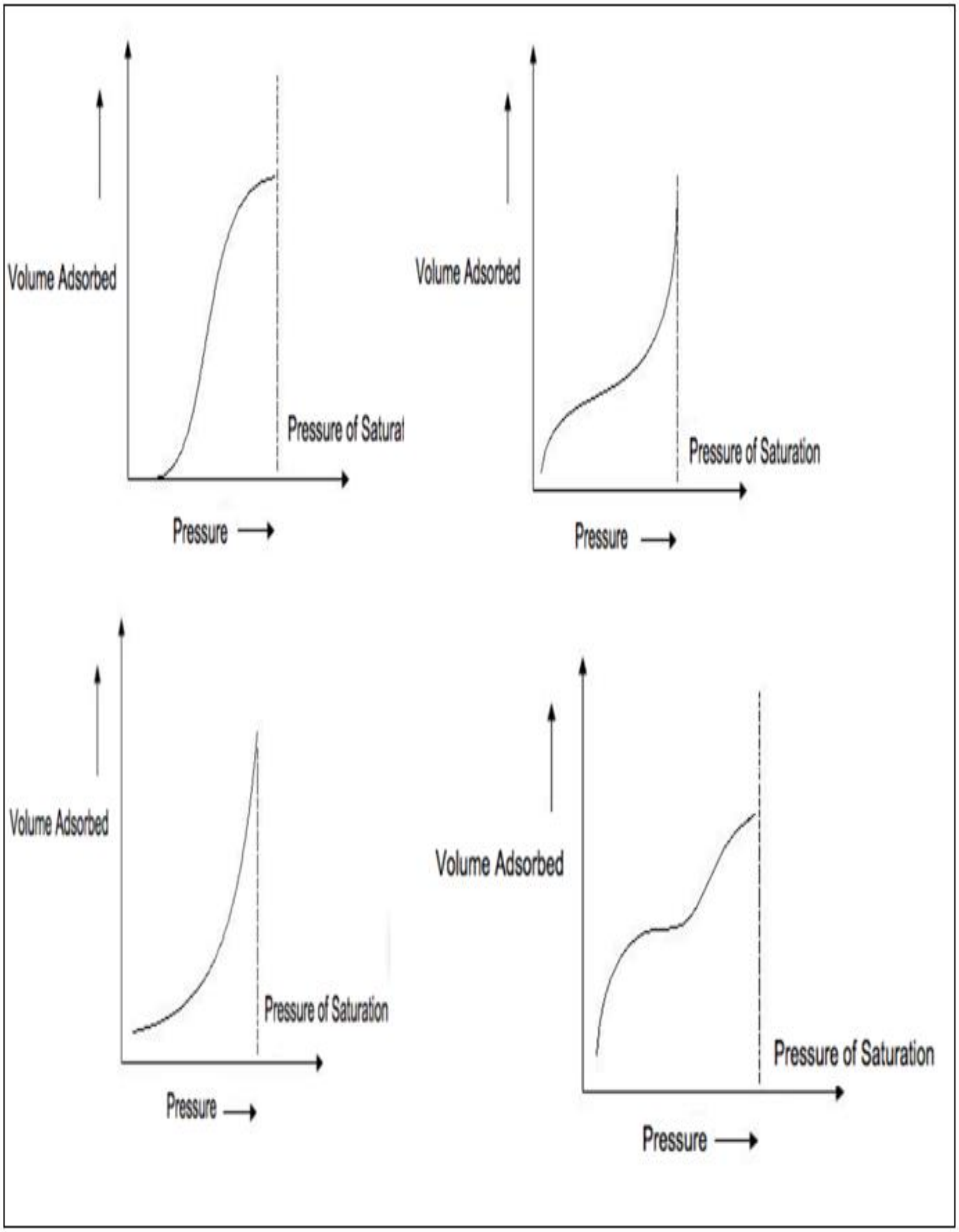
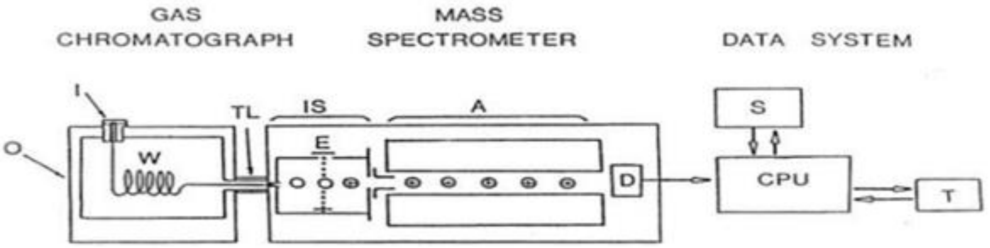


Figure 11: Types of Adsorption Isotherm

3.6 Gas chromatography-mass spectrometry

Chromatography involves the distribution of a desire compound between the two phases one is mobile phase and other is stationary phase. Gas is the mobile phase in GC and stationary phase is an immobile. The sample moves in the capillary tube is called chromatographic or GC column. These columns are made of fused silica and if they covered with polymeric coating they are more durable. Organic compounds require the extraction of organics from the water matrix. The organic compound is injecting into the GC column by few micro liters of the concentrated solvent. Inert gases such as nitrogen, helium and hydrogen are used to sweep the organic compound. Every compound has different solubility's in the liquid phase which travels in the GC column and normally called the retention time. Retention time of higher molecular weight and similar properties of the liquid phase are generally high.

The components come from GC column passes through the detectors and these detectors are called mass spectrometers. A MS detector attaches with the GC column and the combined system are called GC-MS. Mass spectrometer contain the source chamber in which molecules are entered and bombarded by the electrons. Ions are formed which are multiply charged. Ions are separated by their mass to charge ratio in the analyzer section and are detected by an electron multiplier. Plotting between the ions detected and their m/z gives the spectrum which helps to identify the original organic structure. GS-MS figure is shown in below figure **[5].**



(O=Oven, I=Injector, W=WCOT Column, TL=Transfer Line, IS=Ion Source, E=Electron Beam, A=Analyzer, D=Detector, CPU=Central Processing Unit, T=Terminal, S=Data Storage Device)

Figure 12: Schematic of GC-MS Analysis system

Summary

For the testing of catalyst several characterization techniques like XRD, SEM, BET and TGA are used for the prepared catalyst. Scanning electron microscopy is a technique which can be used to find out the structural properties of the crystal. X-ray diffraction (XRD) is the technique to find out the phase of an unknown crystalline material and also the information about the crystal shape and size. EDS was used for the elemental analysis and TGA gives the information about the thermal degradation of the material. Then prepared catalyst is run into Fischer Tropsch synthesis reactor to find out the production of gasoline. The GCMS was done to analyze the composition of hydrocarbons.

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Chapter 4: Experimental Work

This experimental work is divided into two parts. First one, the preparation of activated carbon form Lal Tana leaves and then mixing and preparation of catalyst for Fischer Tropsch synthesis.

4.1 Catalyst Preparation

4.1.1 Preparation of activated carbon

Wasted leaves from "Lal Tana" are collected and then dried in a sunlight atmosphere for 3-4 days and then oven dried at 105℃ for 5hr. Dried leaves are crushed and passed through a sieve of 250µm.H_3PO_4 is used as a activated agent that changed the thermal degradation of the "Lal Tana" tree leaves. H_3PO_4 are increasing the number of defects which anchoring site for metal particles and also increase the surface area. Absorption time of H_3PO_4 (wt 50%) into powder that is collected from dried leaves is 16hrs at room temperature with 3:1 ratio. Then the absorption material is calcined in a box resistance furnace at 500-600℃ for 2 hrs. The produce char is washed with distilled water to remove the excess H_3PO_4 until the neutral ph is attained. Then dried in a oven at 105℃ for 1 hr in order to obtain a activated carbon **[1]**

4.1.2 Preparation of Catalyst

The catalyst were prepared by a wet impregnation method in which the prepared 4 gram activated carbon from "Lal Tana ", are mixed with a 10% of iron nitrate ($Fe(NO_3)_3.9H_2O$) by adding drop wise 10 ml of deionised water. The sample were placed in a room (25° C) for a 24 hr. Finally the sample were calcined in a box resistance furnace at 350℃ for 3 hrs and then dried at 120℃ for one hour **[2].**

4.1.3 Catalyst Reaction

The FT reaction were performed in a fixed bed reactor having a length of 10 cm with a diameter of 3.3 cm. After loading a catalyst into a reactor, then reduction of catalyst are started with a hydrogen gas flow of 30 sccm and nitrogen flow gas (10 sccm), nitrogen gas used as a carrier. After reduction at 450 C for 4-5 hrs then cooling down to 300 C in order to promote the reaction at 20 bar under the presence of H_2/CO ratio 1:1.The product gases collected from separator are analyzed by chromatography and hydrocarbons on carbon basis **[3].**

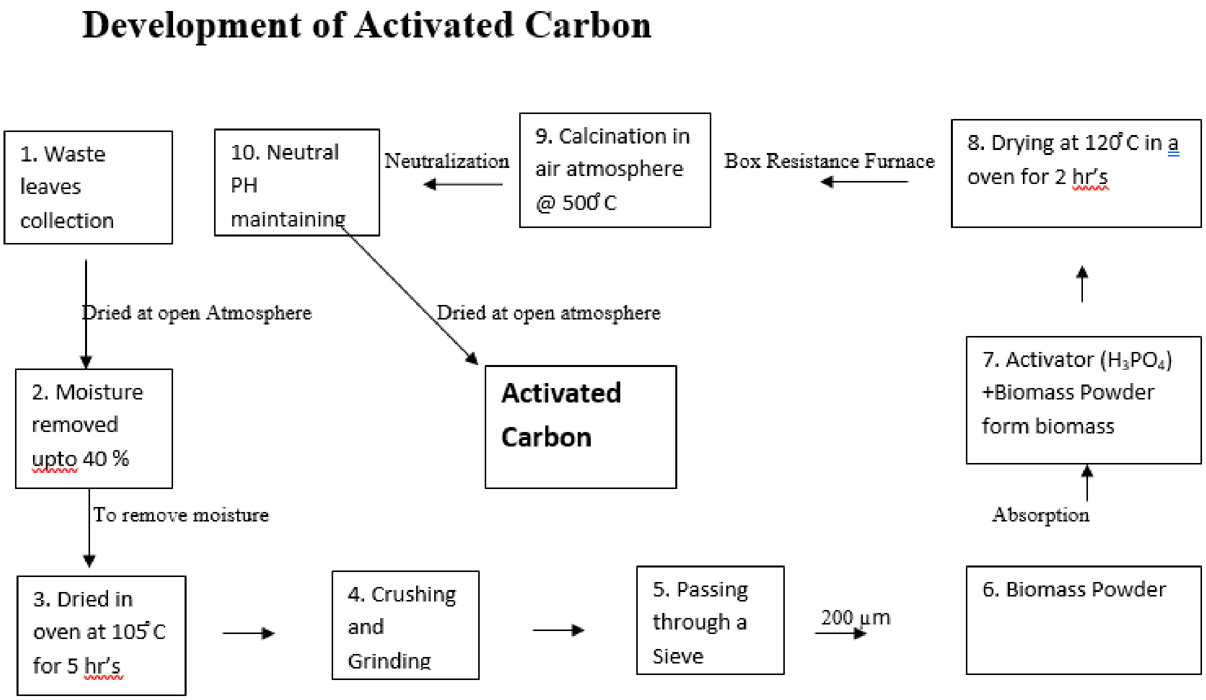

Figure 13: Block diagram of Development of Activated Carbon

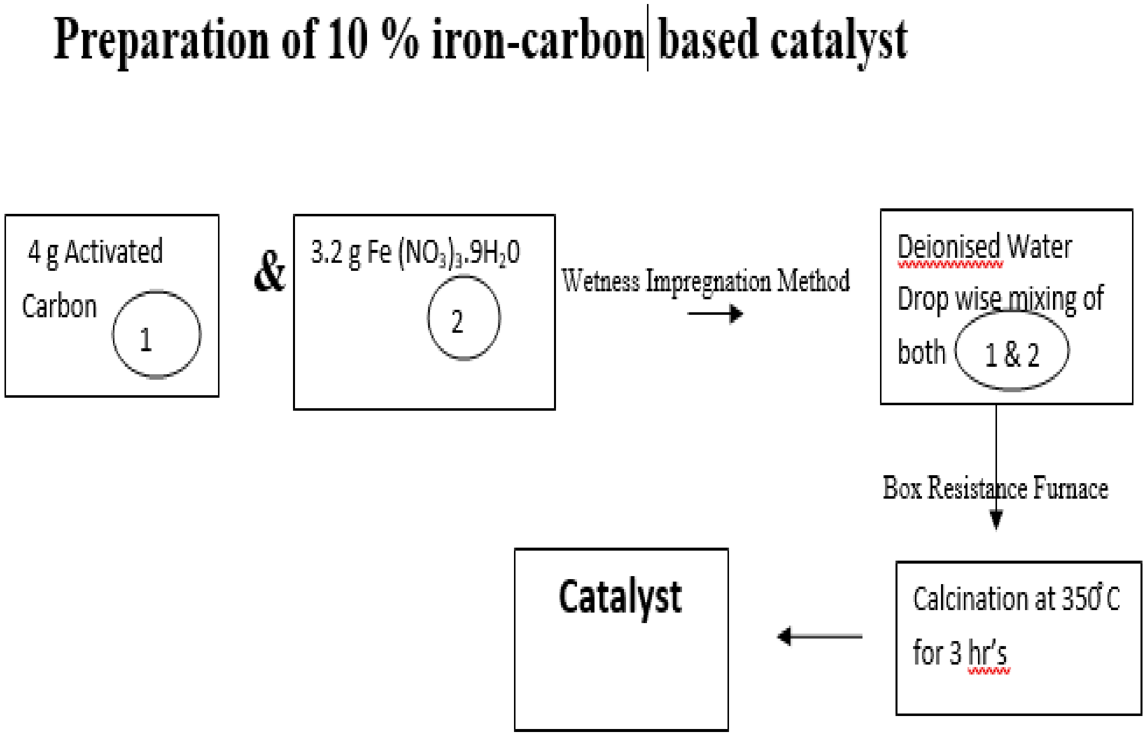

Figure 14: Preparation of 10 % iron-carbon based catalyst

Table 3: List of Catalyst Prepared

Name of Catalyst	Method of Preparation	Promoter
Fe-AC-K	Wet Impregnation	Potassium
Fe-AC	Wet Impregnation	Without Promoter

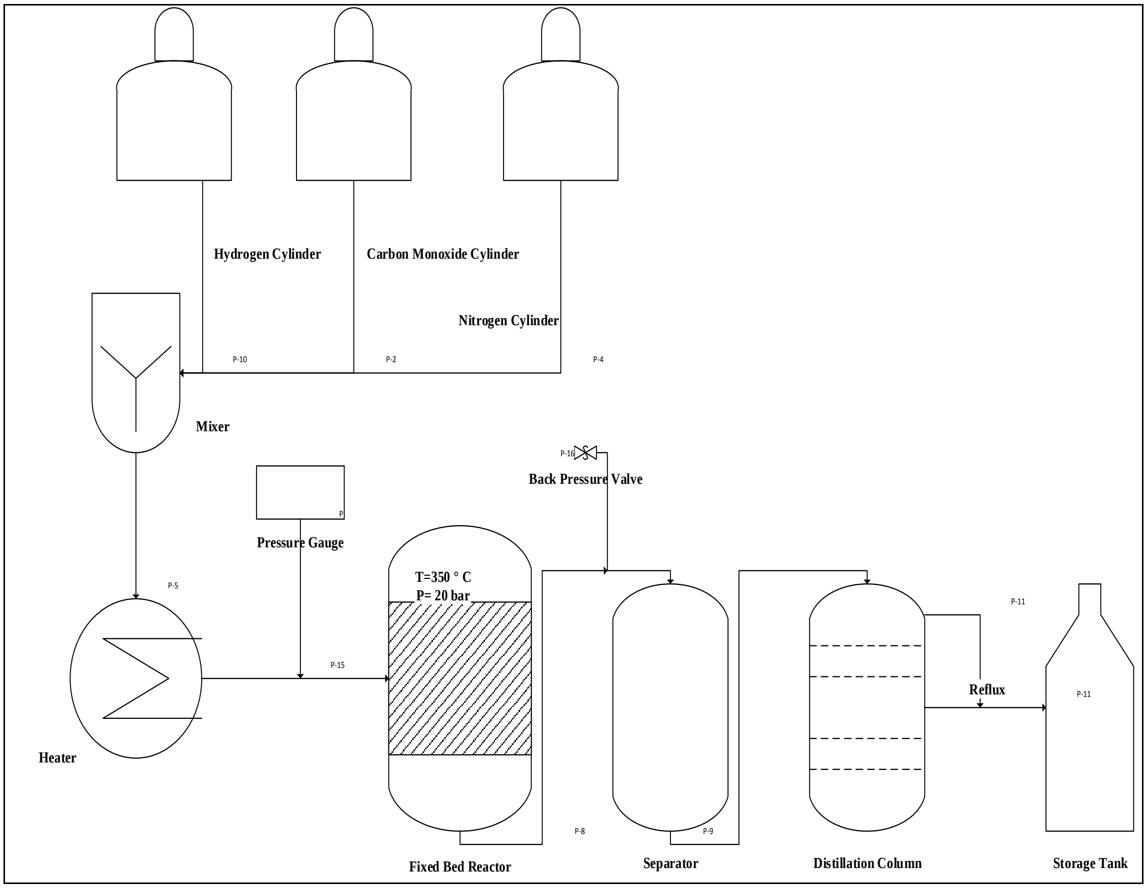

Figure 15: FTS process flow diagram

Table 4 Complete Testing conditions for FTS

Reduction Parameters	**Reaction Parameters**
Temperature = 450℃	Temperature = 350℃
Pressure = 3 bars	Pressure = 20 bars
H_2Flow Rate =30 sccm	H_2Flow Rate = 30 sccm
CO Flow Rate = 0 sccm	CO Flow Rate = 30 sccm
N_2Flow Rate = 10 sccm	N_2 Flow Rate = 10 sccm
Time of Reduction = 6 hours	Time of Reaction = 10 hours
H_2:CO = 1:1	

Summary

This study focused on the preparation of activated carbon and iron based catalyst. For the comparison of synthesis technique and chemical structure of carbon supported iron catalyst in Fischer Tropsch synthesis. Two different catalysts were prepared by wet impregnation method. First catalyst was carbon supported iron catalyst using potassium as a promoter. Second catalyst was also carbon supported iron catalyst using without promoter effect. Both the catalyst were tested in fixed bed reactor at 350℃ and 20 bar pressure for 10 hrs and then compare the results on the basis of C_{5+} selectivity of different hydrocarbons.

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[2] YongweLu,QiangeYan,JnnKan,Baobao Cao, Jason Street,FeiYn,FischerTropsch Synthesis of olefin-rich liquid hydrocarbons from biomass-derived Syngas over carbon-encapsulated iron carbide\Iron nanoparticles Catalyst, Fuel,193,369-384,2017

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Chapter 5: Results and Discussion

5.1 Characterization Results

5.1.1 Scanning Electron Microscopy

Scanning electron microscopy is a technique which can be used to find out the structural properties of the crystal. Scanning electron microscopy of activated carbon prepared from “Lal Tana” is shown in figure 18. The activated carbon is prepared by wet impregnation method. The micrograph images of prepared activated carbon are taken at different resolution. The high resolution image is marked as X10,000 which means that image is taken when subject is enlarged 10,000 times its original size and similarly other images are taken at X5,00 and.X2,000 resolutions. The figure 18 (b, c) shows that activated carbon with porous material is in tubular form shape and figure (d) shows that the sample is swelled during the preparation process due to the phosphoric acid is used as a activator agent. The SEM images of carbon supported iron based catalyst are shown in figure 19. The images are taken at different resolutions X5, 000, X5, 500, X10, 000 and X20, 000 and all the images suggest the formation of needle like structures. At high magnification (20,000) the needles structure are clearly large in size due to the increased in the Fe crystallite size.

The SEM images of carbon supported iron based catalyst with potassium promoter are shown in figure 20. The images are taken at different resolutions X2, 500, X20, 000, X40, 000 and X50, 000. In the images some of the potassium particles are agglomerates with carbon and iron particle and form the globular structure at high magnification. The SEM of post processing carbon supported iron catalyst with potassium promoter is shown in figure 20. The images are taken at different resolutions X5, 000, X10, 000, X15, 000 and X20, 000. The results show that the needle and globular particles are deformed when they are process into the FT reactor at different conditions such like 350℃ for 10 hrs at 20 bar pressure.

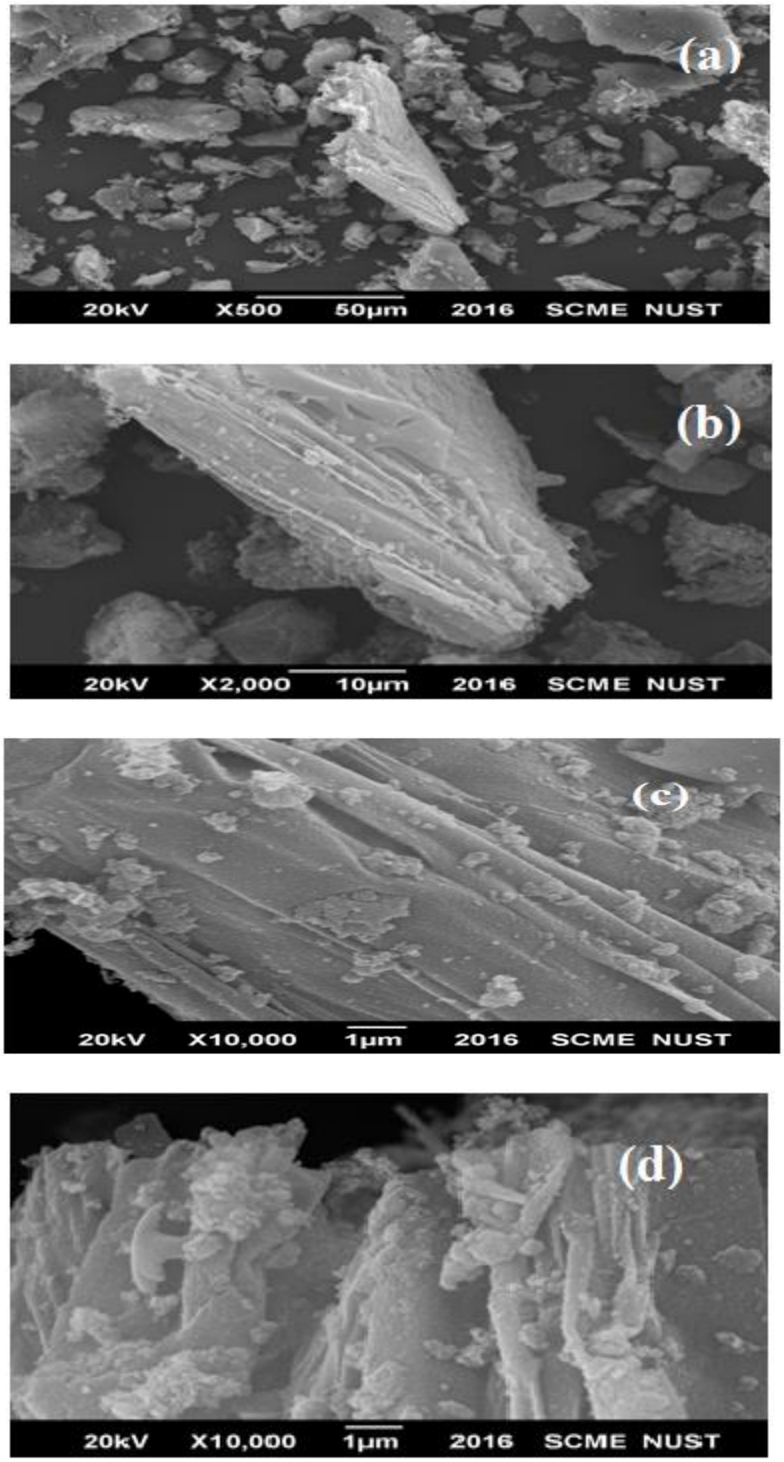


Figure 16: SEM Microscopy of prepared activated carbon from “Lan Tana”

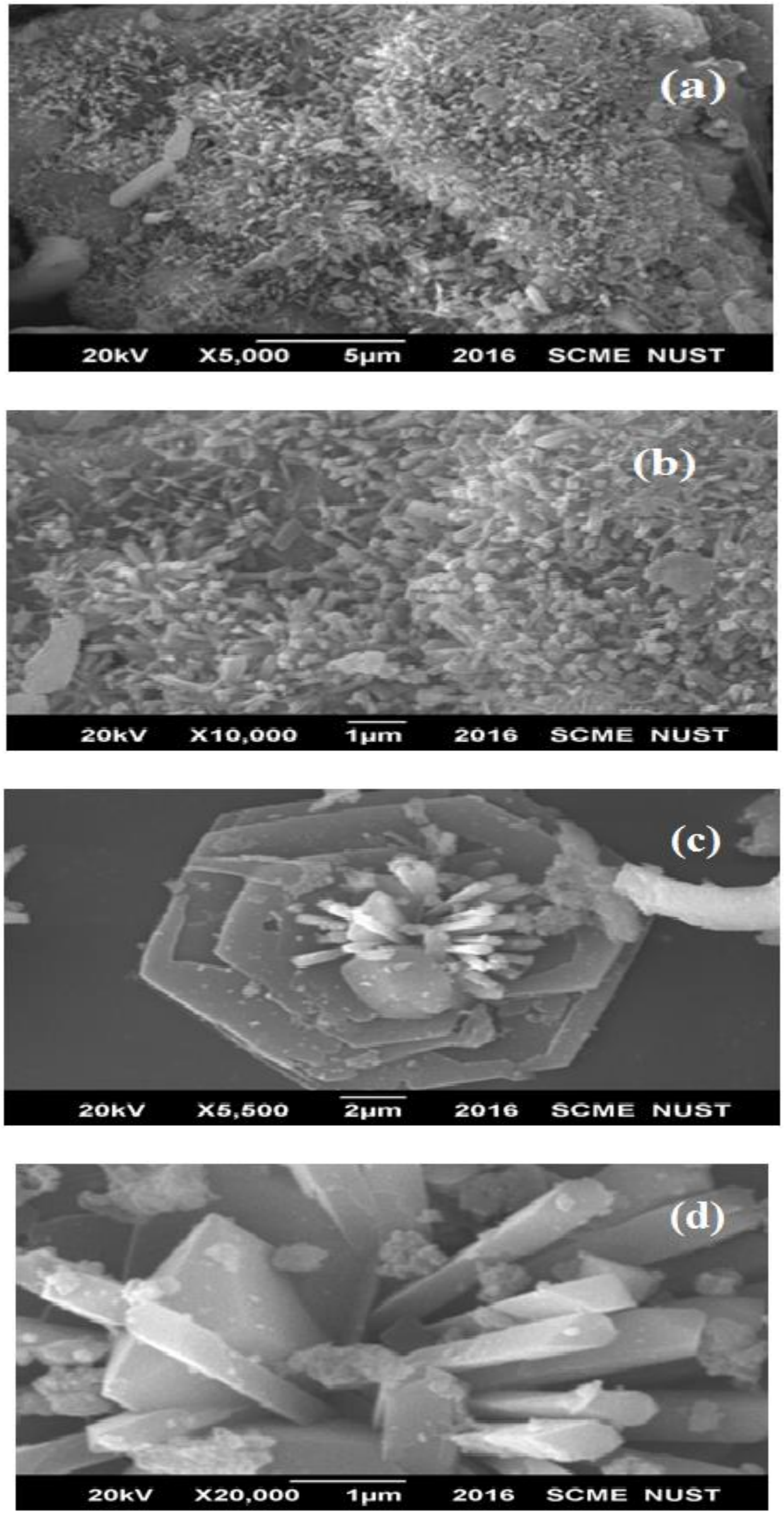


Figure 17: SEM Micrographs of Fe-C catalyst

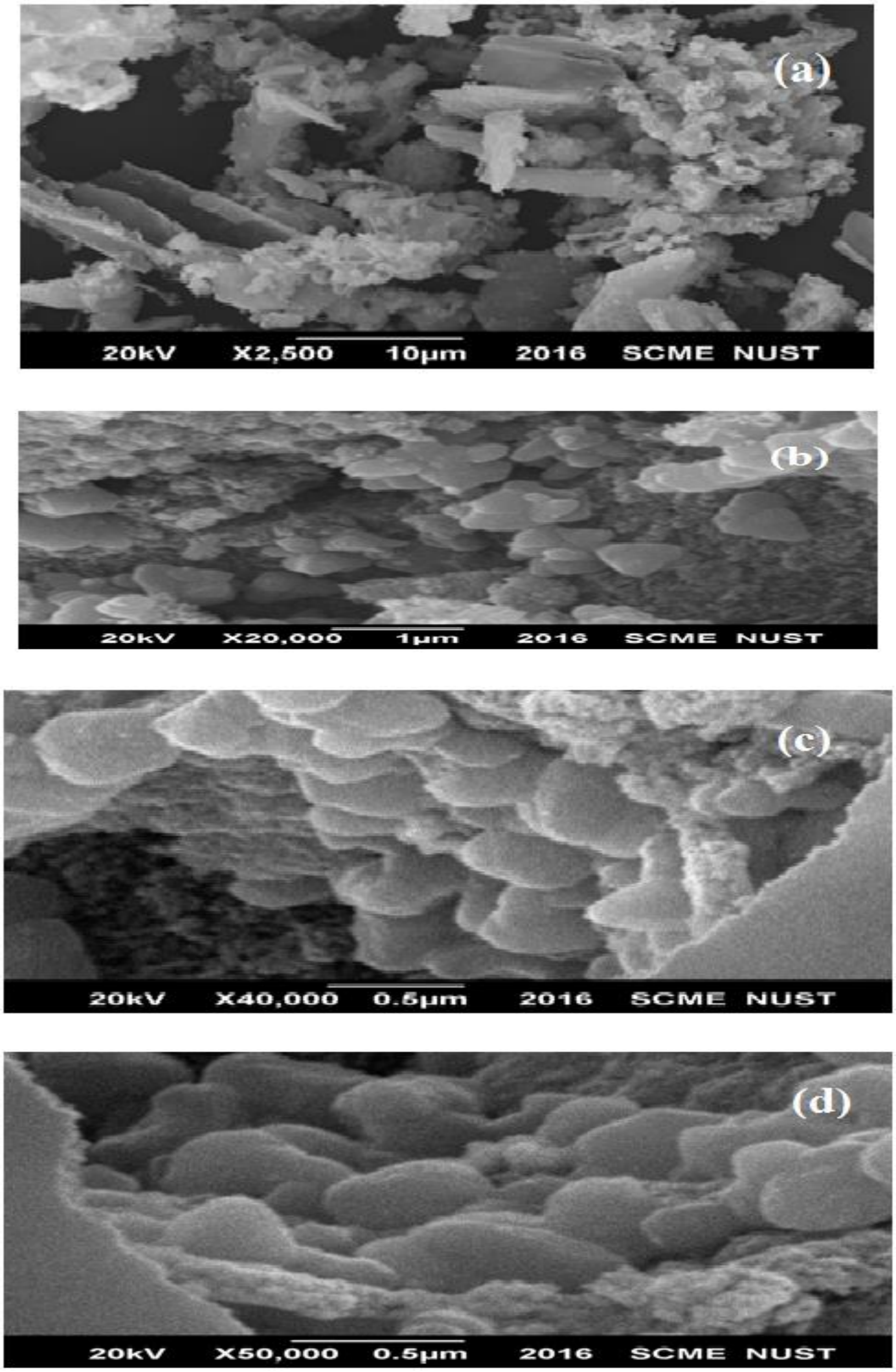


Figure 18: SEM Micrographs of Fe-C-K catalyst

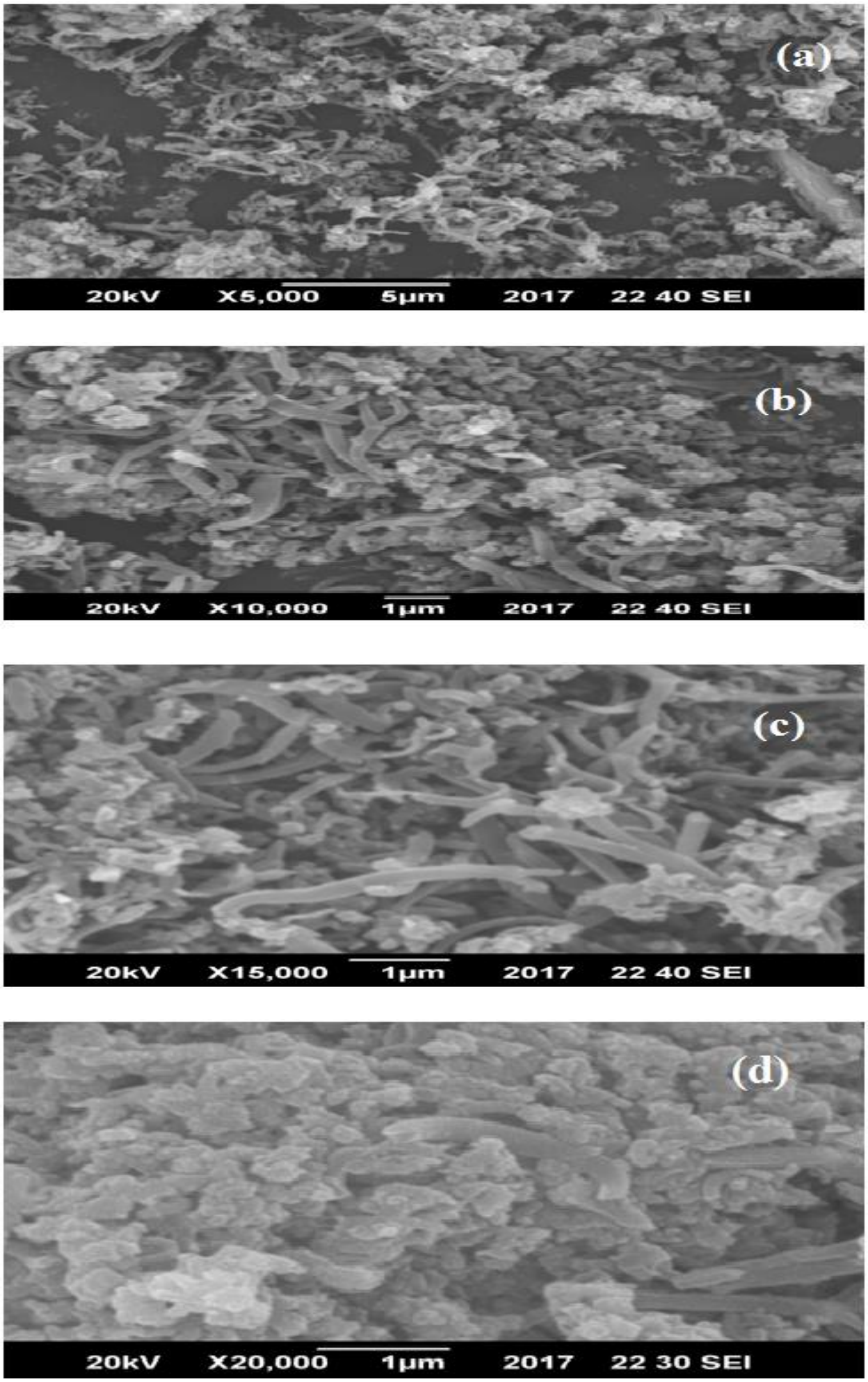
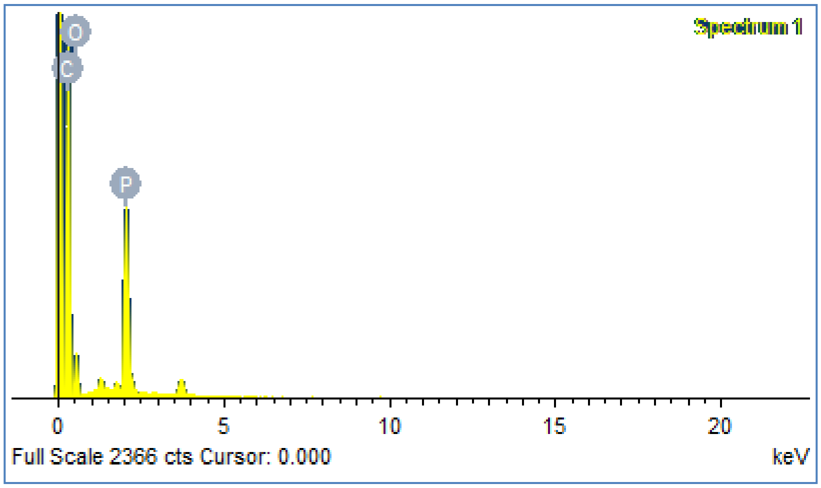


Figure 19: SEM Micrographs of Fe-C-K catalyst (Post used in FTS)

EDS data of prepared activated carbon, carbon supported iron catalyst with and without potassium promoter and catalyst used in FT plant after Fischer Tropsch synthesis (with potassium promoter) are shown in the below table. In the activated carbon the amount of phosphorus is present due to the H_3PO_4 which is used as the activator agent during the activated carbon preparation. In carbon iron supported catalyst (with & without promoter) the amount of oxygen are the confirmation of the oxide formation and these oxygen group are removed during the reduction process (water gas shift reaction). After the catalyst testing in FT plant (carbon supported iron catalyst with potassium promoter) a very small amount of calcium and magnesium are also present due the human error and does the effect the working of catalyst. The detail analysis is shown in below figures.

Table 5: Elemental analysis obtained from EDS

Sample ID	C (%)	P (%)	O (%)	Fe (%)	K (%)
AC "Lal Tana"	77.51	17.85	4.64	___	___
Fe-C	24.64	5.36	38.08	31.92	____
Fe-C-K	17.83	____	49.59	24.82	7.76
Fe-C-K (FT used)	69.85	____	17.06	8.46	3.59



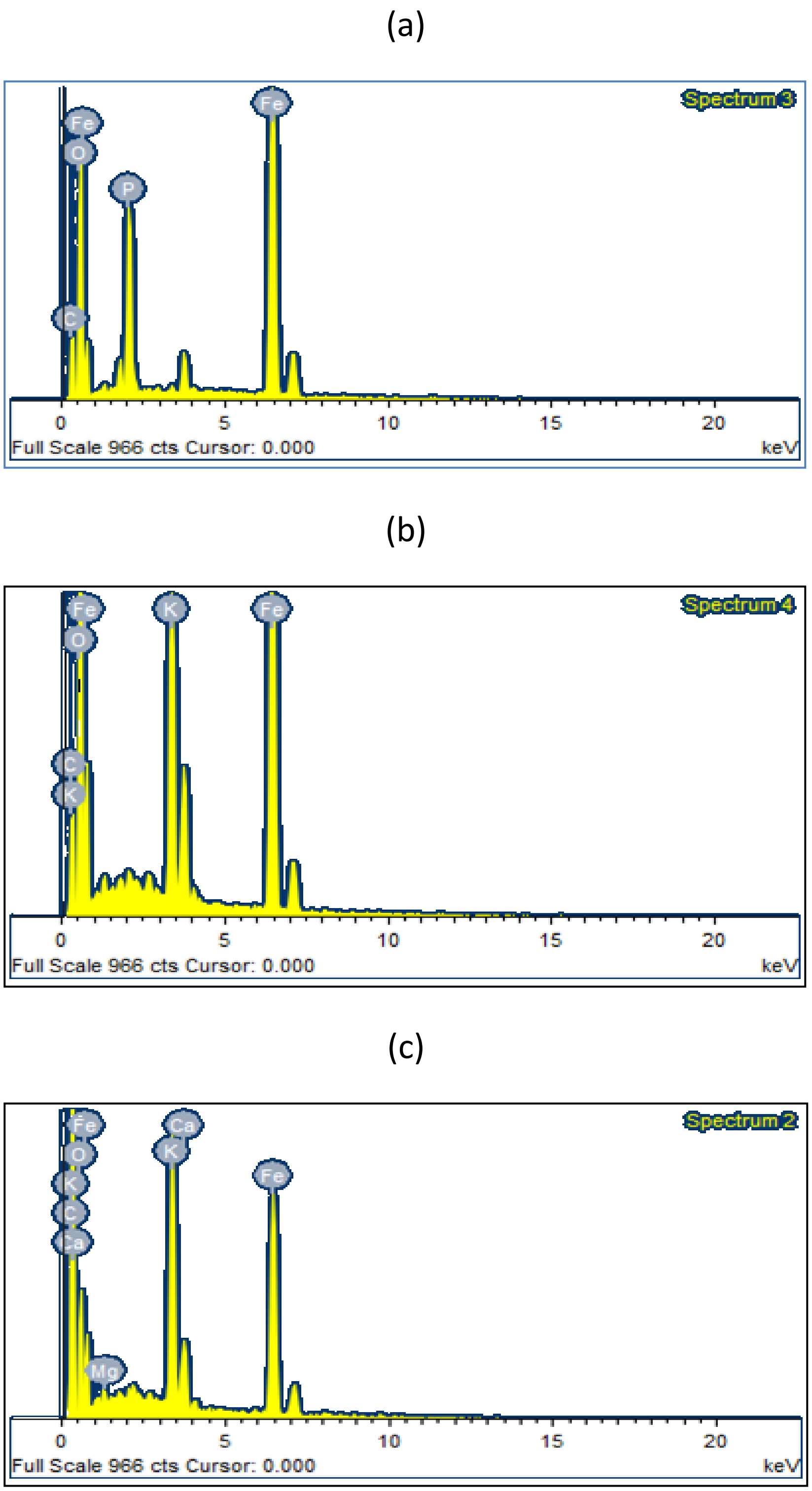


Figure 20: (a) Activated carbon from "Lan Tana" (b) Fe-C catalyst (c) Fe-C-K catalyst (d) Catalyst used in FT plant (Fe-C-K)

(d)

5.1.2 XRD

X-ray diffraction (XRD) is the technique to find out the phase of an unknown crystalline material and also the information about the crystal shape and size. XRD pattern of activated carbon prepared from “Lal Tana” are shown in the figure in which the peak at angle 23° and 43° which revealed the presence of crystalline carbonaceous structure. The sharp peak is produced at angle 23° and 43° due to better layer alignment which is the further confirmation of a crystalline structure. Small number of stacked layer are formed which is shown in the diffraction pattern with broad lines in the prepared activated carbon.

The XRD pattern of the carbon supported iron catalyst with potassium promoter and after Fischer Tropsch synthesis process are shown in figure in which peaks at different angles are formed 24° and 32° which reveals the formation of Fe2O3 and peak at angle 52° presence of the potassium (the peak is small because the amount of potassium is only 3%). After the Fischer Tropsch reaction the peaks at different angles 35°, 44°, and 62° are shows that potassium can facilities the formation of the iron carbide during the FT reaction.

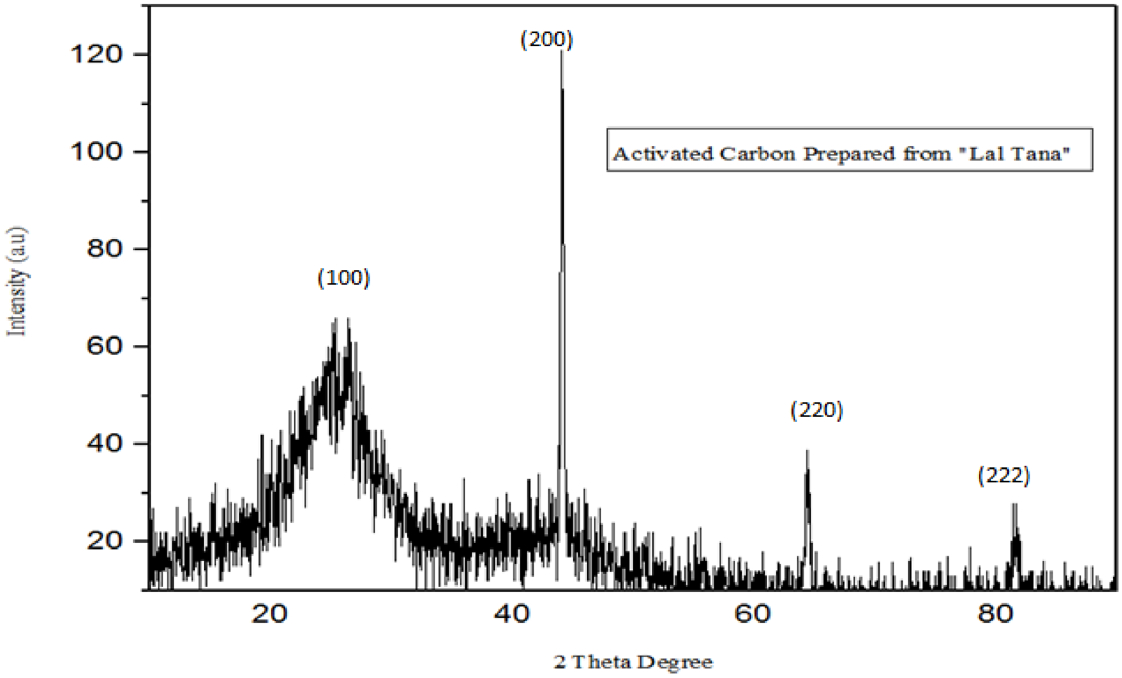


Figure 21: XRD of Activated Carbon Prepared from “Lan Tana”

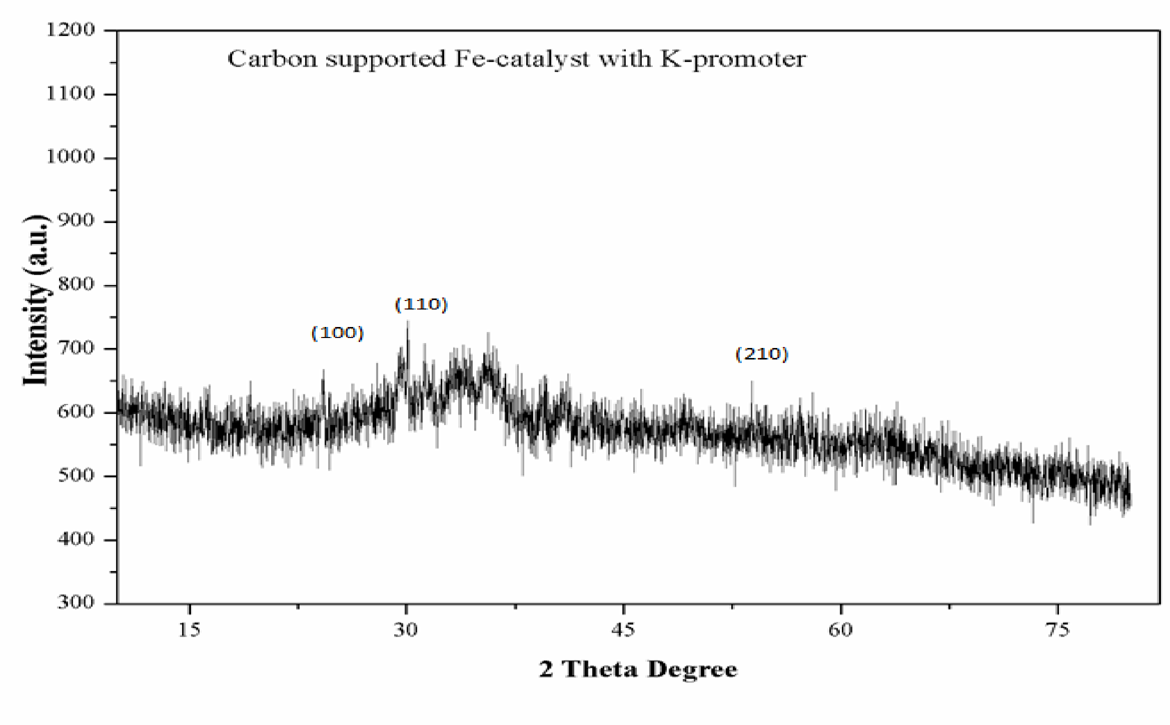


Figure 22: XRD of Fe-C-K catalyst

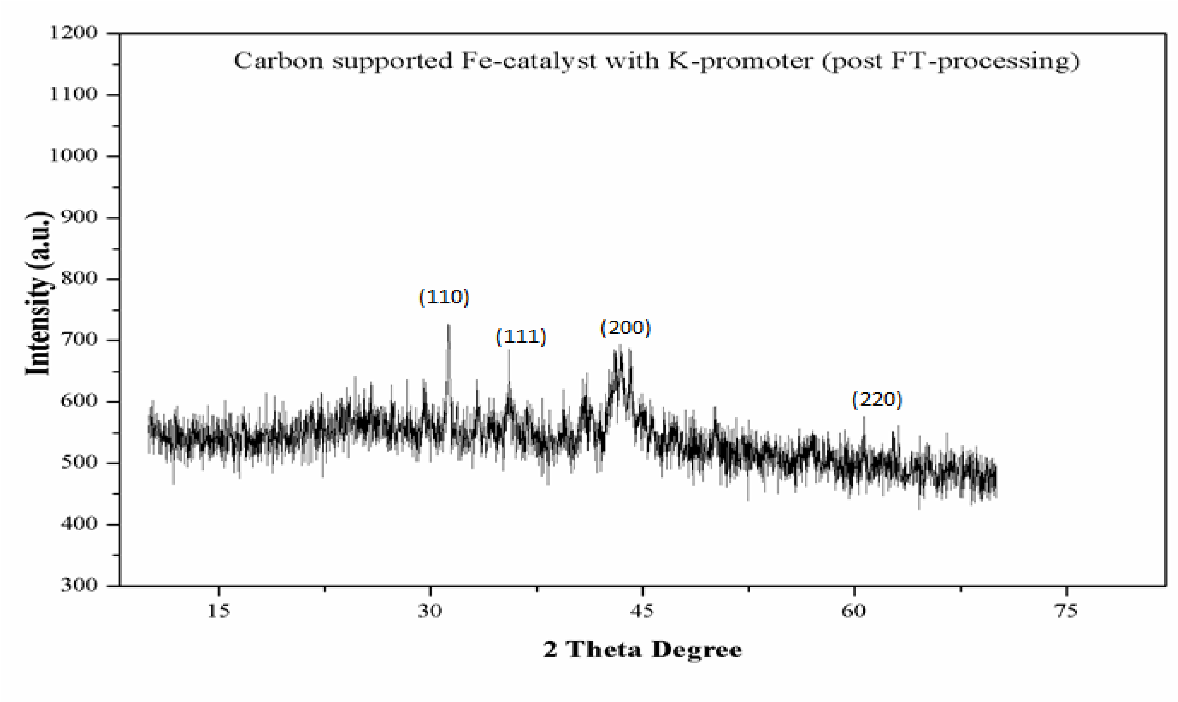


Figure 23: XRD of Fe-C-K post FT processing

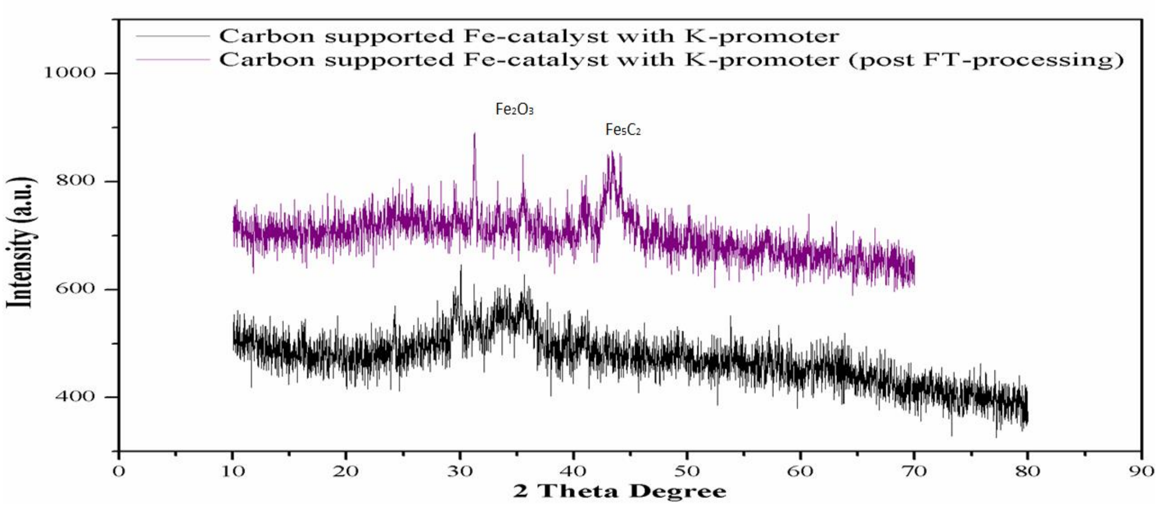


Figure 24: XRD of pre and post Fe-C-K

5.1.3 TGA

Thermalgravitic analysis was done under nitrogen gas atmosphere. The activated carbon prepared from “lal tana” and all catalyst stars their weigt loss range 110-250℃ due to the water molecules in the interlayer space and sharply degarade at 450℃ and fully thermally degraded at above 600℃. The carbon supported iron based catalyst thermally degarded at above 550℃. The catalyst with potassium promoter shows his gradually decrease their weight and deompoise at about 600℃. When the potassium promoter catalyst run into FT plant at certain condition then the behaviour of TGA analsis are changed and sharply degrade at 250℃ and full weight loss at below 500℃.

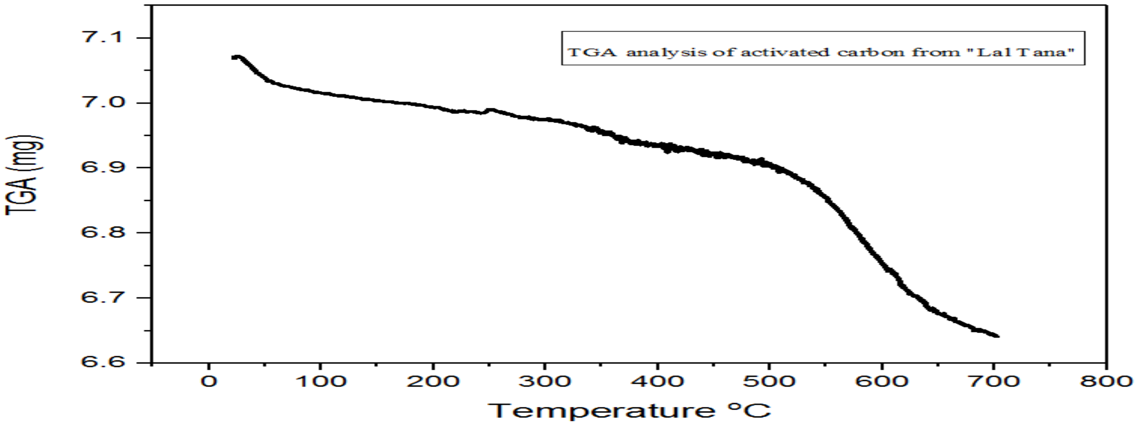


Figure 25: TGA of activated carbon prepared from “Lan Tana”

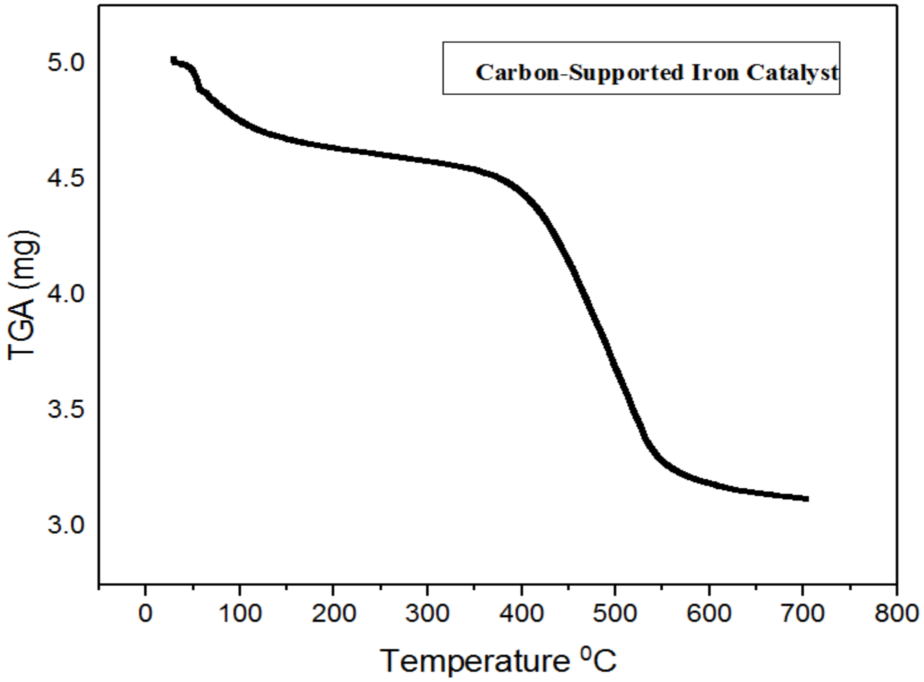


Figure 26: TGA of Fe-C

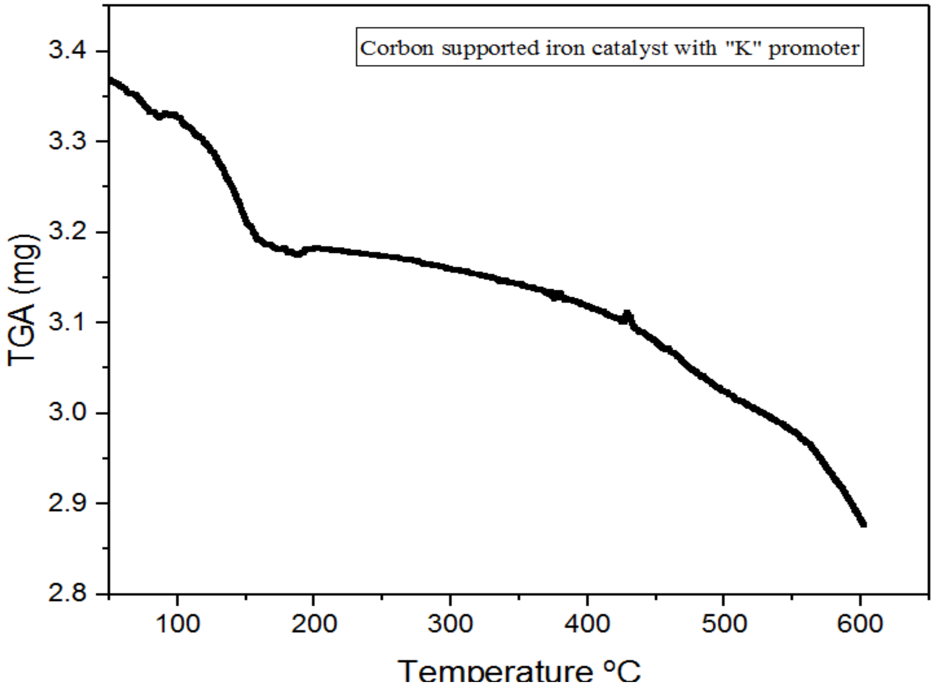


Figure 27: TGA of Fe-C-K catalyt

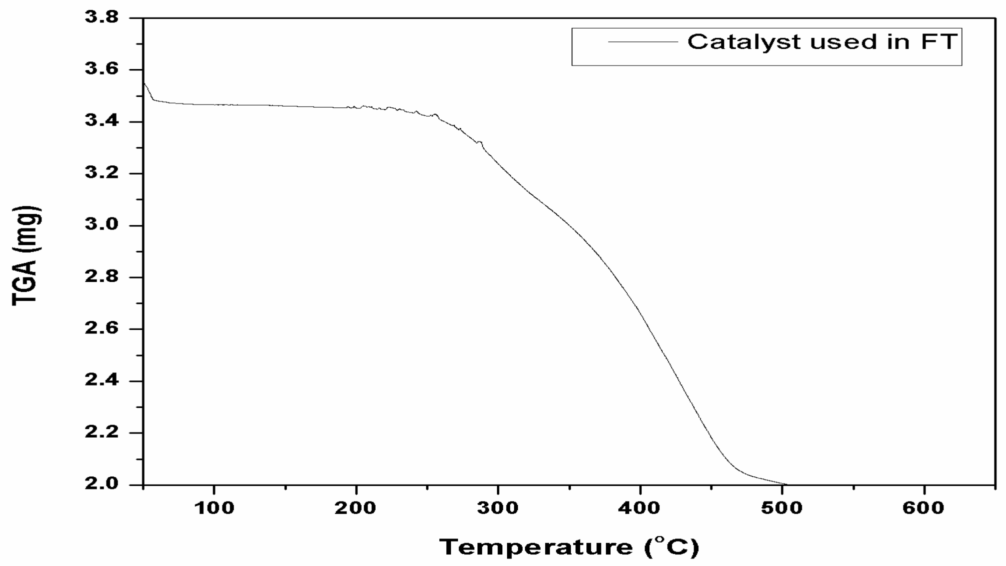


Figure 28: TGA of Fe-C-K catalyst after Fischer Tropsch Synthesis

5.1.4 BET analysis

The surface area of the activated carbon and the carbon supported catalyst were determined by “Micromeritics Instrument Corp” company BET instrument. The surface area of activated is high as compared to the iron based catalyst. The isotherm gives us the information about the porous texture of the solids. The monolayer formation is the prevailing process at relative low pressure and multilayer absorption is take place when the relative pressure is increased.

The thickness of the adsorbate is increased gradually until the condensation point is achieved. The degassing condition of activated carbon 2 hrs at 100° C but the condition of catalysts is 4hr degassing under nitrogen atmosphere at 350℃. The surface area, pore volume, pore size and average particle size are shown in the below table.

Table 6: Surface Area Analysis

Sample	BET surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)	Avg. Particle Size (nm)
AC “Lal Tana”	611.21	0.284	18.62	___
Fe-C	78.74	0.036	27.34	761.966

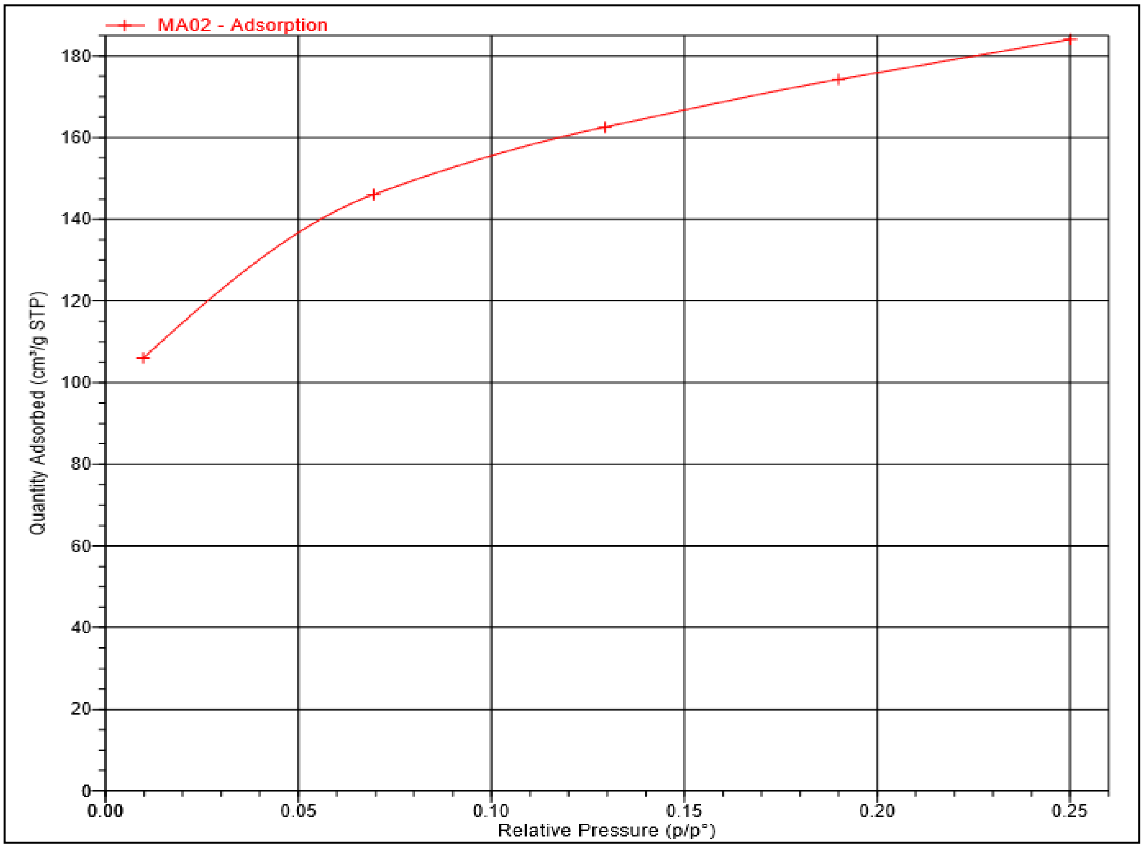


Figure 29: Adsorption isotherm of activated carbon from “olive tree”

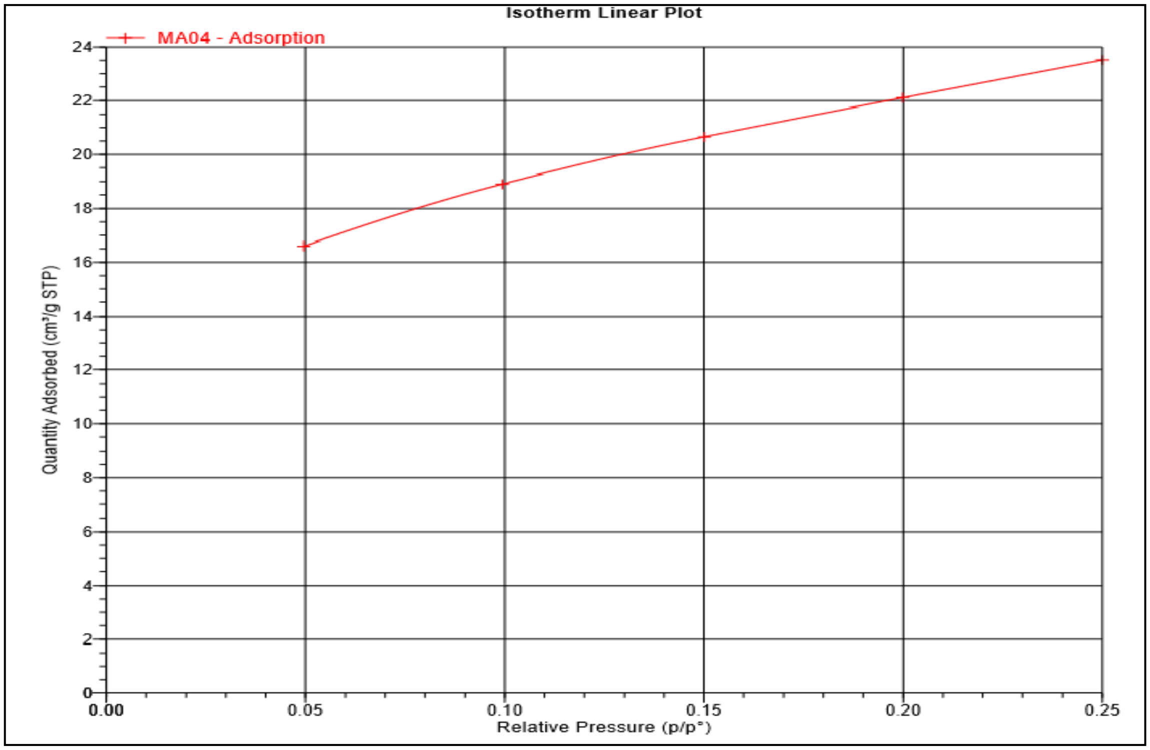


Figure 30: Adsorption isotherm of Fe-C catalyst

5.2 Fischer Tropsch synthesis product analysis

The Fischer Tropsch synthesis was performed by using the carbon supported iron catalyst with potassium promoter. After the reaction sample were collected from separators and sealed into the glass vials in order to avoid the evaporation. There are two separate layers formed clear in the picture, the lower white layer are oxygenates and the upper brown layer are C_5+ hydrocarbons. The GCMS was done to analyze the composition of hydrocarbons. The operating condition are 120℃ the injected temperature and helium is used as a carrier gas at pressure of 89 Kpa and the column flow rate 1.44ml/min with time duration of 30 minutes. The GCMS results shows 76 different peaks and the below table shows the all possible compounds present in the product. The highest quantity of C_8 is much higher than the other hydrocarbons. The total percentage of different hydrocarbons in the mixture is (C_5-C_7) is 9% and (C_8-C_{23}) is 91%.

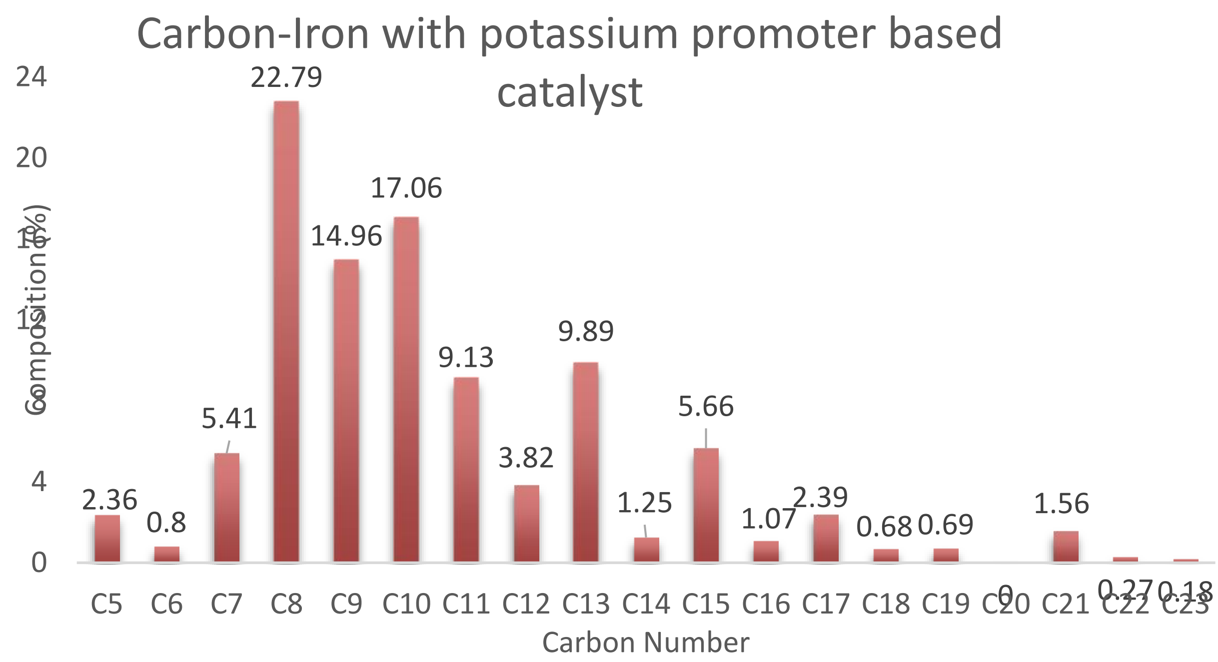


Figure 31: Chain length distribution of Fe-C-K catalyst

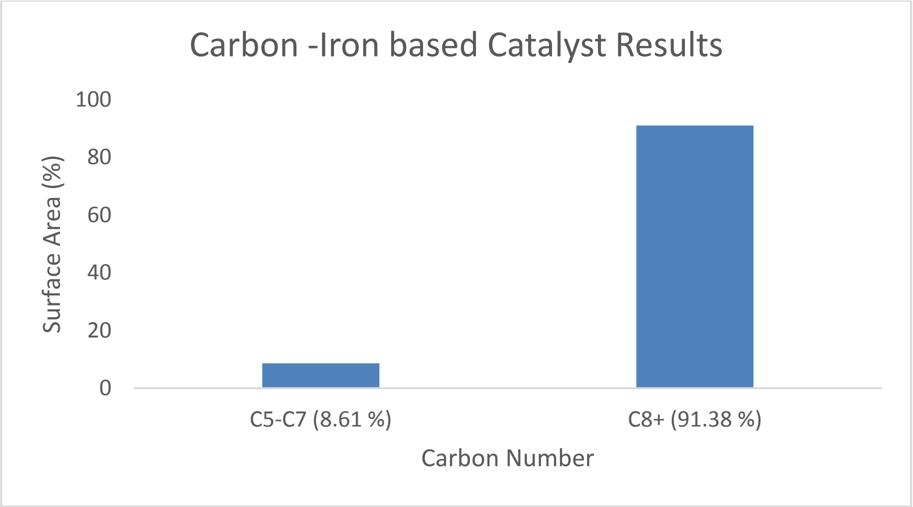


Figure 32: Chain Length Distribution of Fe-C-K Catalyst Results

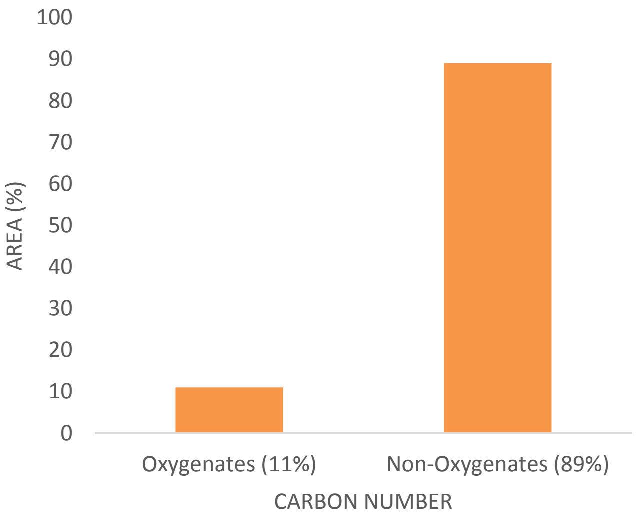


Figure 33: Comparison of Oxygenates and Non-Oxygenates

Figure 34: Product samples from FT process

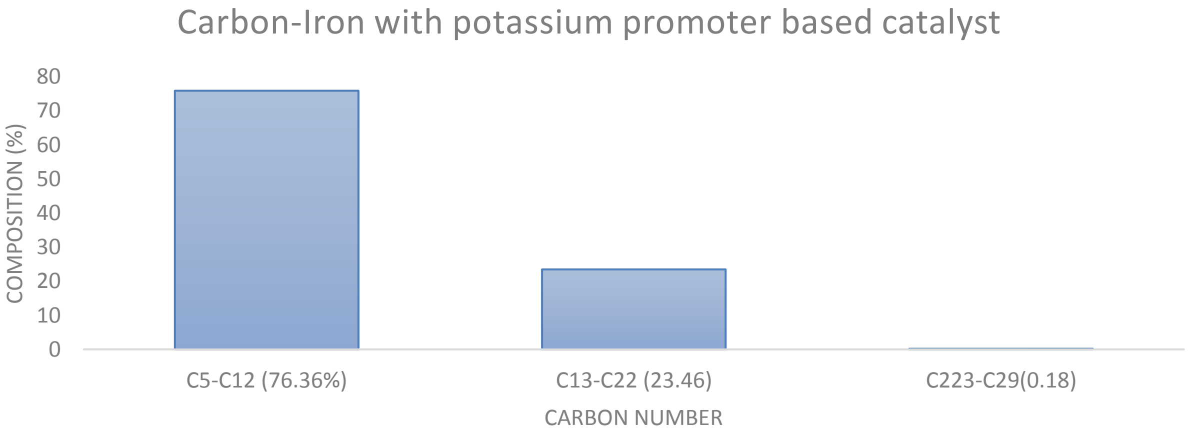


Figure 35: Percentage of chain length distribution by using Fe-C-K catalyst

Table 7: List of compounds in the FT product by using Fe-C-K as a catalyst

Compound Name	**Similarity**	**Formula**	**Mol.wt**	**Area %**	**Height %**
1-Heptene, 3-methyl	85	C_8H_{16}	112	1.45	1.43
1-Octene, 3,7-dimethyl	91	$C_{10}H_{20}$	140	2.61	2.32
1-Butanol, 3-methyl-	90	$C_5H_{12}O$	88	2.36	2.65
Toluene	97	C_7H_8	92	3.64	4.10
1-Hexene, 2,5-dimethyl	84	C_8H_{16}	112	1.51	1.18
1-Octene	97	C_8H_{16}	112	7.46	10.39
Hexane, 2,4-dimethyl	94	C_8H_{16}	114	3.47	3.91
2-Octene, (E)	97	C_8H_{16}	112	0.92	1.20
2-Octene 10	97	C_8H_{16}	112	1.19	0.77
3-Oxatricyclo[3.2.1.0(2,4)]octane	84	$C_7H_{10}O$	138	0.67	0.54
Cyclooctanone	87	$C_8H_{14}O$	126	0.59	0..44
1-Octene, 3-methyl-	90	C_9H_{18}	126	1.10	0.93
1-Octene, 3,7-dimethyl-	91	$C_{10}H_{20}$	140	1.82	1.65
Ethylbenzene	84	C_8H_{10}	106	2.52	2.55
1-Hexanol	90	$C_6H_{14}O$	102	0.80	0.91
p-Xylene	89	C_8H_{10}	106	1.43	1.27
1-Octene, 2-methyl-	93	C_9H_{18}	126	0.43	0.52
2-Heptanone	92	$C_7H_{14}O$	114	0.52	0.61
1-Nonene	96	C_9H_{18}	126	6.58	8.31
Benzene, 1,3-dimethyl	95	C_8H_{10}	106	1.18	1.26
Nonane	94	C_9H_{20}	128	2.85	3.09
2-Nonene, (E)-	94	C_9H_{18}	126	0.86	0.97
2-Nonene, (E)-	96	C_9H_{18}	126	0.53	0.53
Cyclopropane, 1-methyl-2-(3-methylpentyl	87	$C_{10}H_{20}$	140	0.80	0.62
Undecene, 6-methyl-, (Z)-	90	$C_{12}H_{24}$	168	1.05	0.87
6-Methyl-1-(phenylmethyl)-1,2,3,6-tetrahydropyridin-3-ol	81	$C_{13}H_{17}NO$	203	1.05	1.13
Benzene, 1-ethyl-3-methyl-	90	C_9H_{12}	120	1.66	1.10

Benzene, 1-ethyl-2-methyl	97	C_9H_{12}	120	0.59	0.46
1-Heptanol	94	$C_7H_{16}O$	116	0.58	0.65
Nonane, 3-methyl	90	$C_{10}H_{22}$	142	0.29	0.33
Benzene, 1-ethyl-2-methyl-	96	C_9H_{12}	120	0.36	0.39
2-Methyl-1-nonene	92	$C_{10}H_{20}$	140	0.43	0.40
2-Octanone	93	$C_8H_{16}0$	128	0.38	0.40
1-Decene	97	$C_{10}H_{20}$	140	5.23	5.83
1,4-Diphenyl-1-pentanone	75	$C_{17}H_{18}O$	238	0.81	0.62
Undecane	96	$C_{11}H_{24}$	156	2.19	2.16
2-Decene, (E)-	95	$C_{10}H_{20}$	140	0.65	0.65
Cyclopropane, 1-hexyl-2-propyl-, cis-	95	$C_{12}H_{24}$	168	0.60	0.46
Indane	96	C_9H_{20}	118	0.73	0.71
Carveol	69	$C_{10}H_{16}O$	152	1.31	0.57
1,3-Pentanedione, 2,4-dimethyl-1-phenyl-	74	$C_{13}H_{16}O$	204	0.61	0.42
Cyclopentane, 3-hexyl-1,1-dimethyl-	94	$C_{13}H_{26}$	182	0.43	0.35
Benzene, n-butyl-	90	$C_{10}H_{14}$	134	0.57	0.54
1-Octanol	91	$C_8H_{18}O$	130	0.69	0.33
1-Phenyl-1-butene	79	$C_{10}H_{12}$	132	0.60	0.52
Indan, 1-methyl	84	$C_{10}H_{12}$	132	0.54	0.52
1-Undecene	98	$C_{11}H_{22}$	154	4.05	4.15
Undecane	98	$C_{11}H_{24}$	156	1.92	1.77
2-Undecene, (E)-	94	$C_{11}H_{22}$	154	0.68	0.51
Cyclopropane, octyl-	94	$C_{11}H_{22}$	154	0.29	0.30
1-Hexanol, 5-methyl-2-(1-methylethyl)-	78	$C_{10}H_{22}O$	158	0.93	0.31
1H-Indene, 3-methyl-	83	$C_{10}H_{10}$	130	0.55	0.54
1-Tridecene	95	$C_{13}H_{26}$	182	3.43	3.15

Dodecane	98	$C_{12}H_{26}$	170	1.69	1.64
2-Dodecene, (Z)-	96	C_{12}H24	168	0.48	0.46
1-Tridecene	97	$C_{13}H_{26}$	182	2.48	2.35
Tridecane	97	$C_{13}H_{28}$	184	1.55	1.38
1-Tridecene	93	$C_{13}H_{26}$	182	0.34	0.34
1-Pentadecene	97	$C_{15}H_{30}$	210	1.89	1.75
Tetradecane	98	$C_{14}H_{30}$	198	1.25	1.21
1-Pentadecene	97	$C_{15}H_{30}$	210	1.49	1.21
Pentadecane	98	$C_{15}H_{32}$	212	1.24	1.11
1-Pentadecene	96	$C_{15}H_{30}$	210	1.04	0.88
Hexadecane	97	$C_{16}H_{34}$	226	1.07	0.94
1-Heptadecene	98	$C_{17}H_{34}$	238	0.68	0.61
Heptadecane	98	$C_{17}H_{36}$	240	0.90	0.78
1-Nonadecene	97	$C_{19}H_{38}$	266	0.48	0.41
Octadecane	97	$C_{18}H_{38}$	254	0.68	0.65
1-Nonadecene	97	$C_{19}H_{38}$	266	0.21	0.22
Heneicosane	97	$C_{21}H_{44}$	296	0.53	0.52
9-Tricosene, (Z)-	95	$C_{23}H_{46}$	322	0.18	0.16
Heneicosane	97	$C_{21}H_{44}$	296	0.41	0.40
Heneicosane	98	$C_{21}H_{44}$	296	0.43	0.32
Docosane	97	$C_{22}H_{46}$	310	0.27	021
Heneicosane	96	$C_{21}H_{44}$	296	0.17	0.13
Heneicosane	92	$C_{21}H_{44}$	296	0.02	0.03

Summary

Developed a cheap carbon supported Fe based catalyst with potassium promoter for FTS which shows excellent catalytic activity and selectivity toward the desire hydrocarbons. In the activated carbon the amount of phosphorus is present due to the H_3PO_4 which is used as the activator agent during the activated carbon preparation. In carbon iron supported catalyst (with & without promoter) the amount of oxygen are the confirmation of the oxide formation and these oxygen group are removed during the reduction process. Different types of promoter can also be used for FT process in order to increase the C_{5+} selectivity of hydrocarbons. The total percentage of different hydrocarbons in the mixture is (C_5-C_7) is 9% and (C_8-C_{23}) is 91%. Gasoline (76 %), Diesel (23.9 %) and waxes (< 1). Total amount of Oxygenates are 11%.

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Conclusion and Recommendations

Activated carbon with a highly porous structure or surface area is mainly used as an industrial adsorbent and also wastewater treatment purposes. Phosphoric acid (H_3PO_4) is generally used as activator agent that increases the number of defects present in hemicelluloses, which also increase the surface area. H_3PO_4 act as a catalyst in order to promote the bond cleavage reaction and they enhance the cross linking during the reaction through the condensation process. Highly porous activated carbon is used for the gas adsorption in order to make an environment friendly. XRD result shows that, peak a tangle 23° which revealed the presence of crystalline carbonaceous structure. That activated carbon is used for the preparation of carbon supported iron based catalyst by wet impregnation method. Then prepared catalyst is run into Fischer Tropsch synthesis reactor to find out the production of gasoline. The carbon supported iron catalyst with potassium promoter increase the catalyst activity and selectivity toward the desire hydrocarbons. The highest quantity of C_8 is much higher than the other hydrocarbons present in the product sample. The total percentage of different hydrocarbons in the mixture is (C_5-C_7) is 9% and (C_8-C_{23}) is 91%. Different types of promoter can also be used in order to increase the C_{5+} selectivity.

Acknowledgements

In the name of ALLAH, the most merciful, the most beneficent. All praises for ALLAH, the honor of this universe everything in the heaven and earth, glorifies him. He is the one who sent us in the universe among such caring and loving people who are always there for us, whom we can rely, on whom we can trust, who are there when we need them, eager to lighten our pain and shatter our worries away.

Now, I would like to thank our honorable Dean/Principle **Dr. M.Bilal Khan** and Head of the “Center for advanced studies in Energy” (NUST) **Dr.ZuhairS.Khan** who has been very kind to us throughout the study period.

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The time which was spend over here, the practical and conceptual knowledge which we gained made this golden time, of course, a milestone in our professional career with the name of “Center for advanced studies in Energy” a long list of polite cooperative and affectionate professional teachers came across my mind. For whom I confess our negligence of vocabulary to say thanks for their assistance.

Sincerely,

Muhammad Amin

Annex I

International Conference on Recent Innovations in Science, Engineering, Technology and Management (ASAR-ICRISETM-2017) (Accepted)

Development of MOF derived iron catalyst for a Fischer Tropsch synthesis

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Abstract

Metal–organic frameworks (MOFs) are generally used for a gas storage and catalysis applications due to their porous structure formulation. Catalysts are extensively used in different process industries in order to increase the rate of reaction. Iron based catalyst is prepared by a solvothermal method and were annealed in a tube furnace at 550℃ for 3 hours.SEM morphology of metal organic framework is linear in shape and they will be deforming into an oval shape when they were calcined in a tube furnace and become porous structure. TGA analysis of metal organic framework shows that, thermally degradation start at 200℃ and fully degraded at 450℃. BET surface area and pore volume are11.1701 m^2/g& 0.007767 cm^3/g respectively. XRD peaks at 30° shows that the formation of the Fe_3O_4-carbon and that kind of catalyst will enhance the C_{5+}selectivity for hydrocarbons in Fischer-Tropsch process.

Keyword: “Metal Organic Framework; Fischer Tropsch Synthesis; Solvothermal Method”

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1. Introduction

MOFs, they are basically evaluated in heterogeneous catalyst applications due to the reaction applications in liquid as well as in gases phase. They consist of metal ions and organic linkers and they will exhibit a several key advantages with respect to zeolite sand cobalt due to their easy tune able composition [1]. Their huge porosity and storage ability of different unfriendly gases makes them MOF are important. MOFs are prepared through hydrothermal or solvothermal crystallization. Now a day's new methods are established in which high temperature by using conventional electrical (CE) heating system in order to decrease the reaction time and a temperature [2]. Metal–organic frameworks (MOFs) are called with a different names such as porous coordination polymers or networks (PCPs) (PCNs) [3]. Water–gas shift activity in iron based catalyst is highly significant and they received a highly attention of research as well as easy availability and low cost [5].

2. Experimental Work:

Metal organic framework was prepared by literature reported method [4]. In typical method, solution of iron nitrate (Fe (NO3)3.9H2O) 1mmol solution in 5 ml DMF was added to Terephthalic1mmol in 5 ml Dimethyl Formamide. The mixture was stirred in flask for 30 minutes and then it was reacted in autoclave at a temperature of 150°C for 2 hours. After reaction, the sample was cool down to room temperature. The obtained yellow precipitate of MOF was separate by centrifugation method at 4000 rpm for a time of 15 minutes. Washing was performed with Dimethyl Formamide. It was then centrifuged in water and dried in oven at 105°C for 6 hours. For a catalyst preparation the MOF was annealed at 550℃ for a 3 hrs in a tube furnace under nitrogen atmosphere in order to obtain the Fe_3O_4-carbon composite.

3. Results and Discussion:

Results and discussion are carried out with the help of scanning electron microscopy, x-ray diffraction, thermal gravimetric analysis and BET analysis.

a. Scanning Electron Microscopy

SEM morphology of metal organic framework shows linear in shape and the entire iron particles were distributed with a uniform formation. The calcined metal organic framework is deforming into an oval shape due to the removal of all the undesired compounds and become a porous in structure. The distribution made of Fe2O4-carbon composite is aliened.

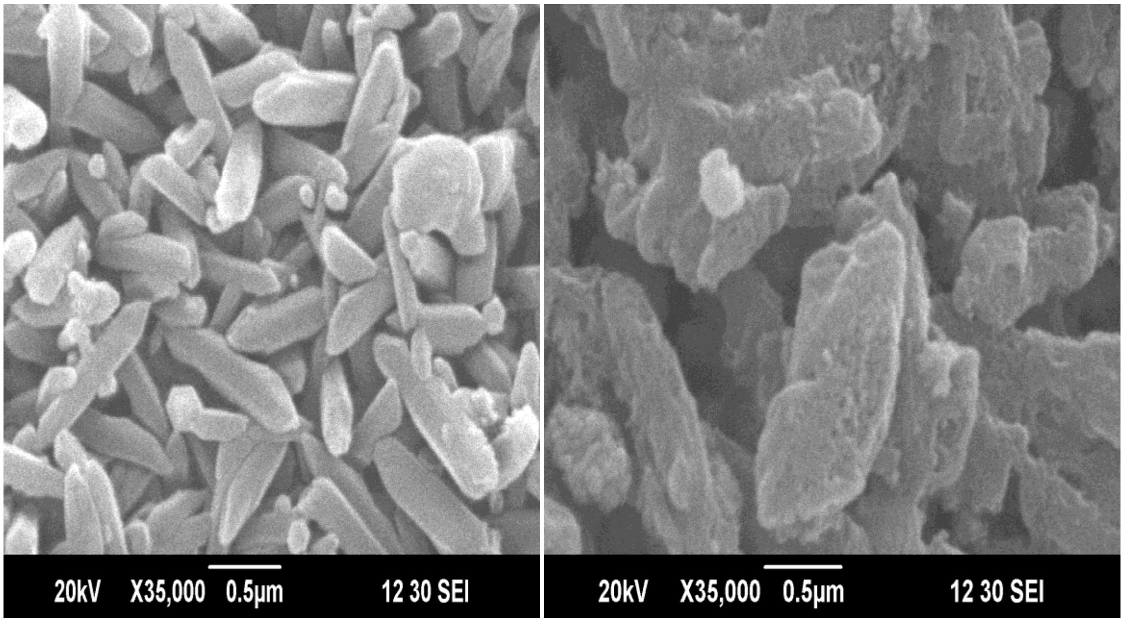

Figure 1 Scanning Electron Microscopy of Fe-MOF

b. X-Ray Diffraction

The XRD spectrum of prepared MOF shows that the peak at angle 9.69˚ is formation of the metal organic framework as similar as MIL-53 and the second XRD peak at angel 17˚ corresponds to a similar peak of MIL-90. Both shows a formation of the iron based MOF.

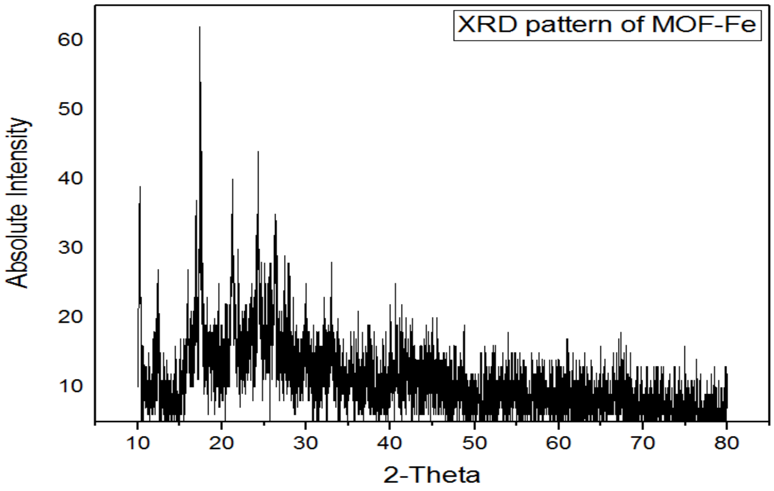

Figure 2: XRD analysis of Fe-MOF

XRD spectrum of calcined catalyst shows that the peak at angle 38˚ is formation of the Fe3O4 structure. The broad spectrum in metal organic framework is due to the stack layer formation.

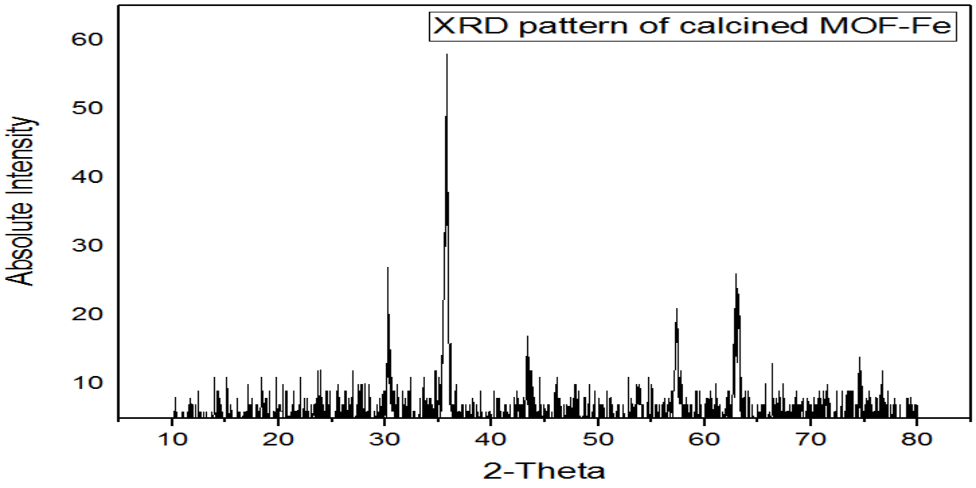

Figure 3: XRD analysis of Fe-Catalyst

c. Thermo gravimetric analysis.

Thermo gravimetric analysis were carried out in TGA 2050 TA equipment from room temperature to 700°C, using a heating rate of 3°C.min-1 under Nitrogen flow (100 mL.min-1). The results shows that metal organic framework will start their thermal degradation at 250℃ and full degraded at 450℃. So calcinations were performing at above 450℃ for three hours.

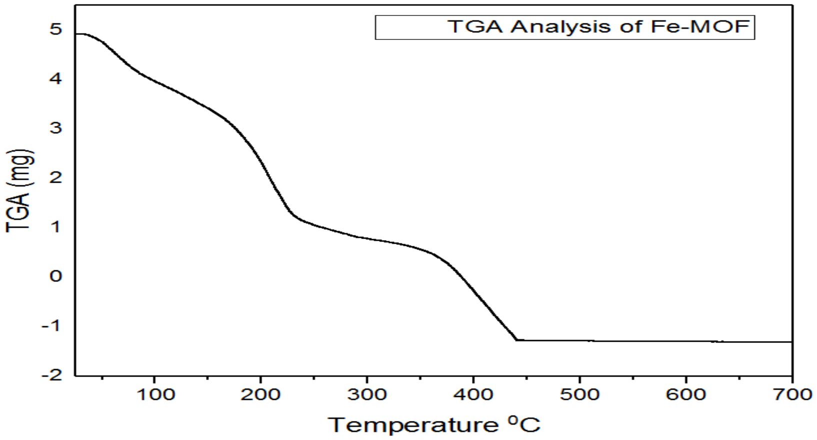

Figure 4: TGA analysis of Fe-MOF

TGA analysis of a calcined MOF shows their gradual degradation at 300℃ and then sharply degrading due to the formation of the Fe_2O_4 carbon composite.

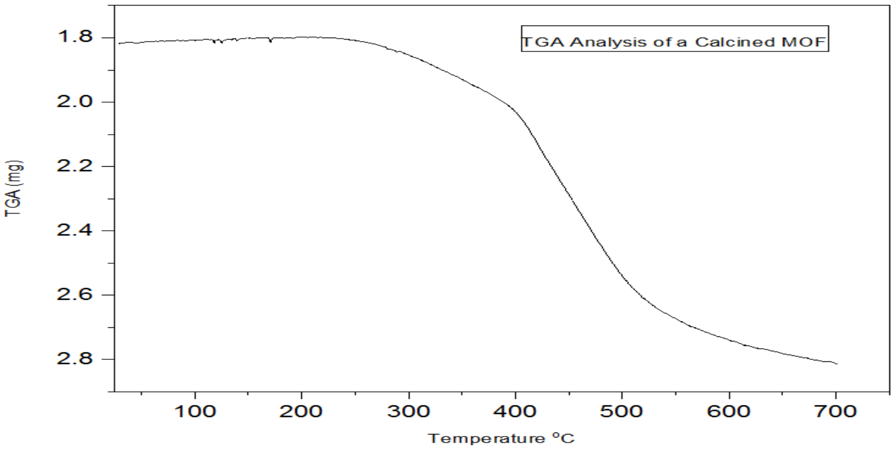

Figure 5: TGA analysis of Fe-Catalyst

d. BET Analysis

BET analysis of calcined metal organic framework were done through Micromeritics Instrument Corp machine with degassing time 3-4 hrs at 350℃. BET surface area and pore volume are 11.1701 m^2/g&0.007767 cm^3/g respectively.

Discussion:

Catalyst with a highly porous structure can be used for gas adsorption and catalysis application. Fe-Catalyst are generally used for a high temperature FT reaction and the above prepared catalyst are will be suitable for HTFT process to get better yield of C_{5+} hydrocarbons. The addition of different promoters like potassium will provide betters results in FT process.

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Annex II

5th International Conference on Phosphorous, Boron and Silicon PBSi-2017 (Accepted)

Synthesis and characterization of activated carbon from olive tree by H_3PO_4 chemical activation

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Abstract

Activated carbon with a highly porous structure or surface area is mainly used as an industrial adsorbent and also wastewater treatment purposes. Activated carbon usually removed chlorine, sediments, volatile organics, taste and order from the water but they are not effective to remove minerals, salts and dissolved inorganic compounds from the water. Phosphoric acid (H_3PO_4) is generally used as activator agent that increases the number of defects present in a hemicelluloses and act as a catalyst to promoting the bond cleavage reaction. They enhance the cross linking during the reaction through condensation. Phosphoric acid were thermally degrading the hemicelluloses structure present in an olive tree and create the porous formation. XRD result shows that, peak a tangle 23° which revealed the presence of crystalline carbonaceous structure. In SEM, result shows that cylindrical units has deformed after the activation. Brunauer-Emmett-Teller(BET), surface area analysis has done through Micromeritics Instrument Corp machine, the total surface area are corresponding to 167.4715 m^2/g and adsorption average pore width are 27.3125 Å. Thermal gravimetric analysis shows that the prepared activated carbon starts their degradation from 200℃ and fully degraded at above 500℃.

Keywords: Activated Carbon, Catalyst, Phosphoric Acid

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1. Introduction

Activated carbon with a high surface area is used for wastewater treatment and gas adsorption. Preparation of activated carbon is carried out into two steps carbonization and activation. Activation is further divided into chemical and physical. When raw material is wood then chemical activation method is used and that is a single step process. Activated carbon produces from olive leaves shows micro-pores structures. Activators are KOH, H_3PO_4, zinc chloride and potassium carbonate etc is generally used. When using H_3PO_4 as an activator then we create pore structure activated carbon. Results shows preferable carbon content through microstructure morphology, finding shows that carbon content is increased from 46 to 74 percent due to the cellulose crystalline structure was destroyed.H_3PO_4 is used as activated agent that changed the thermal degradation of the olive tree leaves. H_3PO_4 are increase the number of defects which anchoring site for metal particles and also increase the surface area.H_3PO_4 act as a catalyst promoting the bond cleavage reaction and promoting the cross linking through cyclization and condensation.

2. Experimental Work

Wasted tree leaves of “olive” are collected and then dried in the presence of sunlight atmosphere for 3-4 days and then put into a oven dried to remove the remaining moisture content at 105℃ for 5hr. Dried leaves are crushed and passed through a sieve of 250µm. A very fine powder in greenish color is obtained. Then H_3PO_4 is used as a activated agent that changed the thermal degradation of the olive tree leaves. H_3PO_4 are increasing the number of defects which anchoring site for metal particles and also increase the surface area. Absorption time of H_3PO_4 (wt 50%) into powder that is collected from dried leaves is 16 hrs at room temperature with 1:1 ratio. Then the absorption material is calcined in a box resistance furnace at 500-600 C for 2 hrs. We collect a char and convert into a activated carbon with the help of washing (distilled water) and maintain the neutral ph. Then dried in a oven at 105 C for 1 hr in order to obtain a activated carbon.

3. Characterization Techniques

Morphology of the activated carbon is analyzed by scanning electron microscopy and crystal structure through XRD. The elemental composition is find out through EDS.

3.1 SEM (Scanning Electron Microscopy)

In SEM, result shows that cylindrical units has deformed after the activation. The pore structure of activated carbon is expanding when phosphoric acid is used as a activator agent. The amount of fixed carbon is produced when volatiles matters are removed due to carbonization and activation. The micropore presences are present which contributes towards the gas adsorption in future.

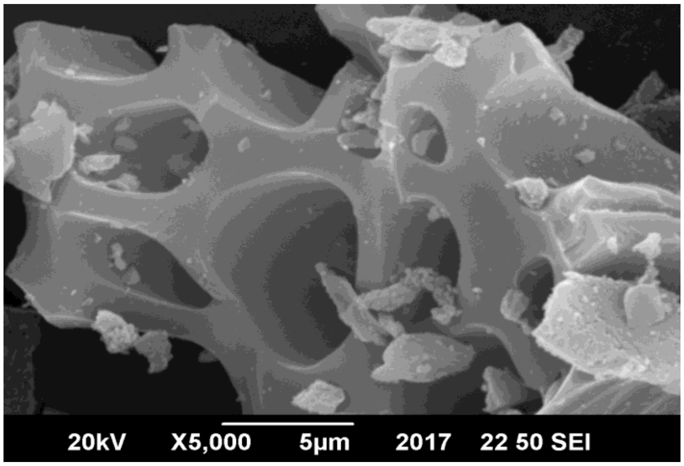

Figure 1: Scanning Electron Microscopy of olive activated carbon

3.2 X-ray Diffraction (XRD)

XRD result shows that, peak at angle 23° which revealed the presence of crystalline carbonaceous structure. If layer alignment is better than sharp peak is produced and that shows crystalline structure is produced. Stacked layer of activated carbon is produced due to the exothermic reaction of water and acid.

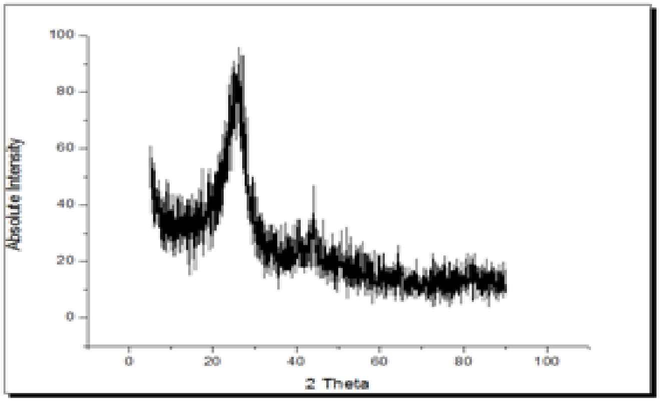

Fig.2 X-ray Diffraction (XRD) of Olive tree

3.3 Thermo gravimetric Analysis (TGA)

Thermal gravimetric analysis shows that the prepared activated carbon starts their degradation from 200℃ and fully degraded at above 550℃.

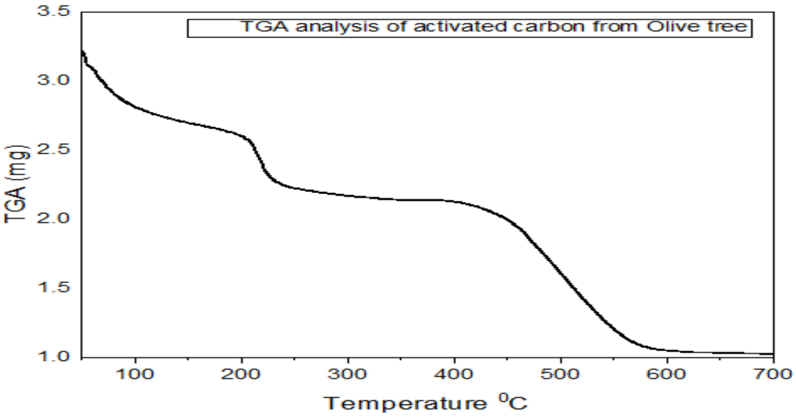

Fig.3Thermo gravimetric Analysis (TGA) of Olive tree

3.4 Elemental Analysis:

EDX analysis shows that the presence of carbon in a prepared sample is greater than 75%which reveal that the part of cellulose crystalline structure was destroyed during process and resulting activation. A little amount of Phosphoric is also present.

Table 1 : Elemental Analysis Obtained from EDS

Sample ID	C	O	P
Olive –Activated Carbon (Weight)	77.51	17.85	4.64

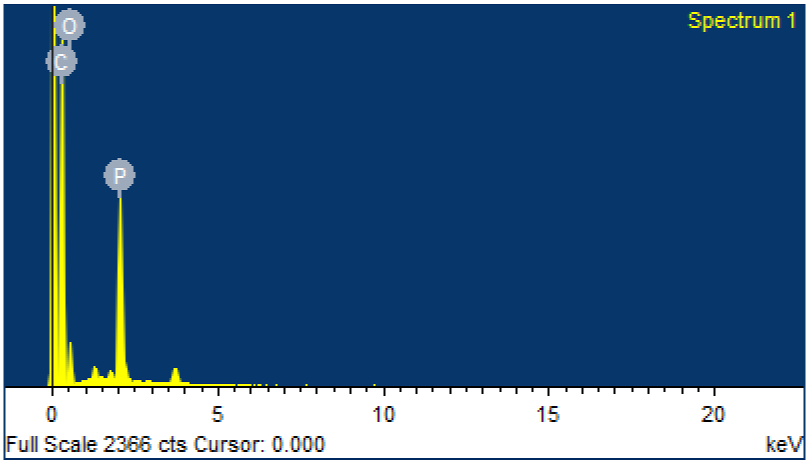

Figure 4: Elemental Analysis of activated carbon obtained from Olive tree

4. Conclusion

Phosphoric acid (H_3PO_4) is generally used as activator agent that increases the number of defects present in hemicelluloses, which also increase the surface area. H_3PO_4 act as a catalyst in order to promote the bond cleavage reaction and they enhance the cross linking during the reaction through the condensation process. Highly porous activated carbon is used for the gas adsorption in order to make a environment friendly .KOH, zinc chloride and potassium carbonate are also used as a activator agent but Phosphoric acid will produced better results. Thermal gravimetric analysis shows that the prepared activated carbon starts their degradation from 200℃ and fully degraded at above 500℃. Activated carbon made from olive tree has a significant porous structure and will start their thermally degradation at 200℃ and loss their major weight at 400℃ which is economical good for the formation of the activated carbon. Further, different activator agents like KOH, zinc chloride and potassium carbonate etc are used to studies the effect of activation on olive tree is recommended in future.

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