

**DEVELOPMENT, CHARACTERIZATION AND  
EVALUATION OF HIERARCHICAL ZEOLITE FOR  
HYDROTHERMAL LIQUEFACTION OF SYNTHETIC  
WASTE WATER TO  
BIO-OIL**

**A MAJOR PROJECT REPORT**

*Submitted in partial fulfillment of the  
requirements for the award of the degree*

of

**Master of Technology**

in

**CHEMICAL ENGINEERING**

**(With Specialization in Process Design Engineering)**

By

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**May 8, 2019**

## CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this dissertation, Entitled “**Development, characterization and evaluation of Hierarchical Zeolite for Hydrothermal Liquefaction of Synthetic waste water to Bio-oil**”, submitted in partial fulfillment of the requirement for award of the degree of **Master of Technology in Chemical Engineering** with the specialization in **Process Design Engineering (PDE)**, is an authentic record of my own work carried out under the supervision of **Dr G. Gopalakrishnan**, Senior Associate Professor, Department of Chemical Engineering, University of Petroleum & Energy Studies, Dehradun.

**Date - 8<sup>th</sup> May 2019**

**Place – Dehradun**

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Dated: 8<sup>th</sup> May 2019

Place: Dehradun

  
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## ABSTRACT

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Bio-fuel will be one of the important energy sources in the upcoming future. Now a days as energy scarcity is one of our primary concern, increased waste generation rate is another burning issue that must be considered. Hydrothermal Liquefaction can provide the solution for both the problems by converting the generated wastes into the bio-fuel. The term "hydrothermal" used here refers to the processing of biomass in aqueous slurries at elevated temperature and pressure to facilitate the chemical conversion of organics of biomass into useful fuels or chemicals. As Hierarchical Zeolite is hydrothermally stable and has both micro and meso-pores on it, it can facilitate the Hydrothermal Liquefaction very efficiently. So this project work involves direct synthesis, modification by incorporating Fe, Co and Fe-Co and characterization of Hierarchical Zeolite and evaluate its catalytic activity for hydrothermal liquefaction of synthetic waste water into low oxygen containing bio-oil.

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## ABBREVIATIONS

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<i>ZSM</i>	Zeolite Socony Mobil
<i>HTL</i>	Hydrothermal Liquefaction
<i>XRD</i>	X-Ray Diffraction
<i>MLD</i>	Millions of Liters per day.
<i>SDA</i>	Structural Directing Agent
<i>BET</i>	Brunauer-Emmett-Teller

# 1. INTRODUCTION

---

Population and industrial growth have increased the demand for energy. World and India primary energy consumption were 13,511 and 753 million toe respectively in 2017 thus making India the third largest consumer next only to China and USA. The share of fossil fuels share of total primary energy consumption of the world continue to be over 80% resulted in CO<sub>2</sub> emission of 32.5 giga tons in the year 2017 alone and its cause of global warming is at alarming rate. The growth in automobiles have increased the consumption of petroleum derived fuels namely motor spirit and diesel resulting in fast depletion of petroleum and its cost escalation. The world proven petroleum reserve as per available 2017 statistics was 1.7 trillion barrels; annual consumption was 33.6 billion barrels and thus expected to last only for 50.8 years. To address the twin sustainability issues of long-term availability of fossil fuels and global warming, diversifying the energy basket and increasing the share of renewable energy is the only option. Among the options of renewable energy such as solar, wind, tidal, biofuels etc., the biofuels is of very important as they have potential to sustain two billion vehicles already on the road which cannot be scrapped for the want of fuels. Important categories of biofuels are bioethanol, biodiesel, biogas and bio oil.

## 1.1 Bioethanol

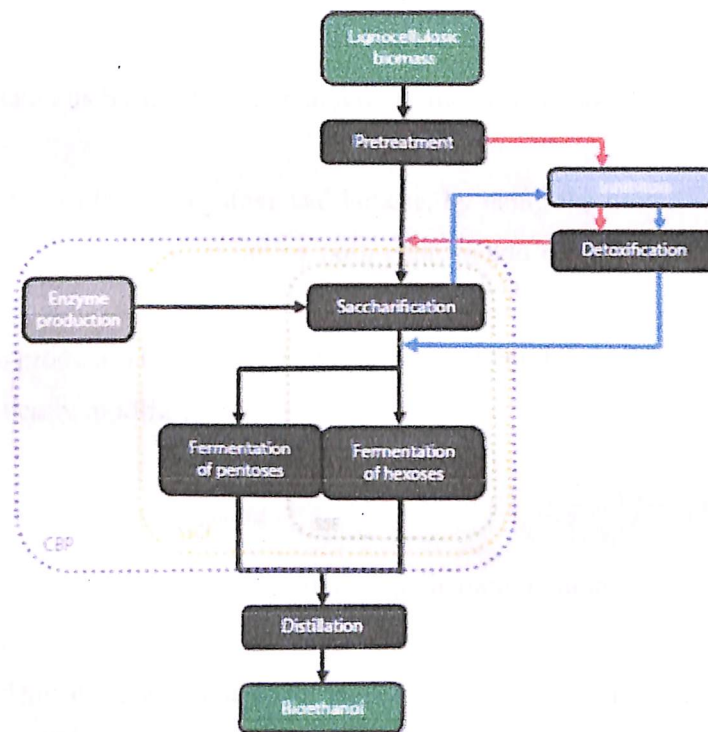
Among the biofuels, bioethanol a substitute for gasoline demands carbohydrates as biomass feedstock employing biochemical conversion [1,2]. In most of the countries, bioethanol of 5 -25% is blended with gasoline used in the regular cars while 85-100% ethanol can be used in flex-fuel vehicles and thus bioethanol is the future fuel for vehicles powered by SI engines. First generation bioethanol is mainly produced from food based biomass namely sugars and starch and thus endangers the food security.

Second generation bioethanol is produced from non-food biomass mainly lignocellulosics which is the largest natural form of carbon available on the earth. Important sources of lignocellulosics are agricultural residues, wood residues, grasses etc. The two routes for the conversion of lignocellulosics are biochemical and thermochemical route.

### 1.1.1 Biochemical Conversion

Biochemical route to convert lignocellulosics to bioethanol involves four major steps;

- Pretreatment to free lignin from lignocellulose
- Enzymatic hydrolysis of lignocellulose to fermentable sugars
- Fermentation of sugars into ethanol.
- Separation and purification of products by distillation, dehydration and rectification



**Fig 1:** Processes for the conversion of lignocellulosics to bioethanol [3]

Accordingly, the following are the integrated biochemical routes to convert lignocellulosics to bio-ethanol.

#### 1.1.1.1 Separate Hydrolysis and Fermentation (SHF)

This method involves chemical or enzymatic hydrolysis of pretreated lignocellulose carried out separately from fermentation step. The main advantage of SHF is that each of this step can be carried out at optimum condition but expensive. [4]

#### 1.1.1.2 Simultaneous Saccharification and fermentation (SSF)

In this method, concurrently saccharification and fermentation are carried out in a single reactor and hence reduced cost. The other important advantage of this process is that the sugars are converted into ethanol quickly, due to which its accumulation is minimized as they are the major inhibitors for the conversion. But the major drawbacks are its inability to control process parameters as optimum conditions for saccharification and fermentation are different and demanding higher amount of exogenous enzymes.

#### 1.1.1.3 Simultaneous Saccharification and co fermentation (SSCF)

This method ferments both pentose and hexose, by using the mixed yeast culture. A single microbe capable of assimilating both pentose and hexose sugars in an optimal way and can also be used to produce a high sugar conversion and ethanol yield [5] but these microbes needs to genetically modified.

#### 1.1.1.4 Consolidated Bioprocessing

It is an in situ method in which all three steps namely cellulase enzyme production, hydrolysis of cellulose to sugars and fermentation are carried out in a single reactor and a single step. Thus there is a significant reduction in the cost but main drawback is the non-availability of a robust organism to produce cellulases with high yield ethanol.

The important drawbacks of biochemical route of bioethanol production from lignocellulosics are that, it only converts the carbohydrates part biomass into the bio-ethanol, *lack of robust pretreatment method to exclude lignin and components other than carbohydrates from biomass* and only a maximum yield of 3 to 4% ethanol necessitating energy intensive distillation step for its purification.

### 1.1.2 Thermochemical Conversion

Bioethanol production from syngas is an emerging technology and it can utilize whole lignocellulosic feedstocks including lignin. First, the biomass is converted to syngas by gasification with oxygen and/or steam. The syngas is catalytically converted into a mixture of shorter alcohols, mainly ethanol and methanol, at 300 °C and a pressure of 69 bar, over Cobalt, molybdenum, rhodium, and some other multi-component catalysts. The yield of ethanol was reported to be 60% [6].

### 1.2 Bio-diesel

Bio-diesel has become one of the attractive biofuels as its blending of 25% with petroleum-derived diesel can be used as fuel in vehicles powered by CI engines and is produced from oil-bearing biomass [8,9]. The biomass is pretreated and by mechanical pressing to extract the oil and then transesterified with methanol to get biodiesel, which is Fatty Acid Methyl Esters (FAME).

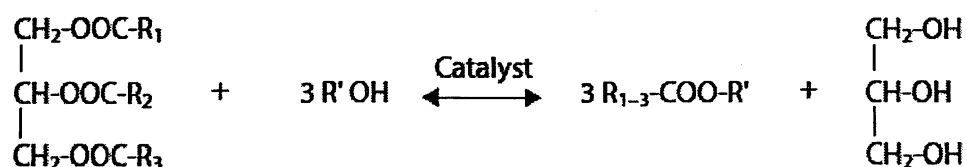


Fig 2: Transesterification reaction

Biodiesel is mainly produced using alkaline catalysts such as sodium or potassium hydroxide due to the short reaction time required, but this process is energy intensive; difficulty of glycerol and catalyst, generation of large volume of wastewater. Acid catalysts such as sulfuric, hydrochloric, or sulfonic acid are also used to produce biodiesel, but these reactions typically have low reaction rates; the acidic environment is a challenge for reactor design; and high alcohol to oil ratios are necessary [7].

Transesterification can also be catalyzed by the enzyme lipase and its important advantages are less energy intensive, efficient, produces less waste water and no soap formation and the disadvantage is the high cost of enzymes. The alternative method for catalytic transesterification is supercritical process for producing Bio-diesel in which the catalyst is eliminated. This uses methanol at supercritical state at higher temperatures and pressure to react with the lipids to produce the bio-diesel. The main

advantage of this process is that free fatty acids are transformed into methyl esters, instead of forming into soap.

### 1.3 Bio-Gas

Biogas upon purification gives biomethane which is potential substitute for natural gas and hence an important gaseous biofuel.

Anaerobic Digestion is the technology which is being practiced for decades for the production of Bio-gas. It is one of the oldest alternative fuel generation technology for efficient waste management which is still in use. It is a biological process which converts organic wastes such as biomass, sewage sludge etc into biogas under the action of microorganisms. The biogas which is formed contains around 60% of methane, 30% of carbon dioxide and traces of hydrogen sulphide. This is a cost effective and economical viable process. This biological treatment is used to treat both industrial as well as domestic wastewater because it is capable enough to support higher volumetric loadings and low nutrient content.

Anaerobic digestion takes place in four steps. In the first step, the biopolymers are broken down into small polymers which is referred as hydrolysis. In second step the monomers are converted into volatile fatty acids with the help of acidogenic bacteria which is called acidogenesis. In the third step, volatile fatty acids are converted into acetic acid, carbon dioxide (CO<sub>2</sub>) and Hydrogen (H<sub>2</sub>) by acetogenic bacteria which is called acetogenesis. Finally, the acetic acid is consumed by methanogenic bacteria and thus producing methane, which is called methanogenesis.

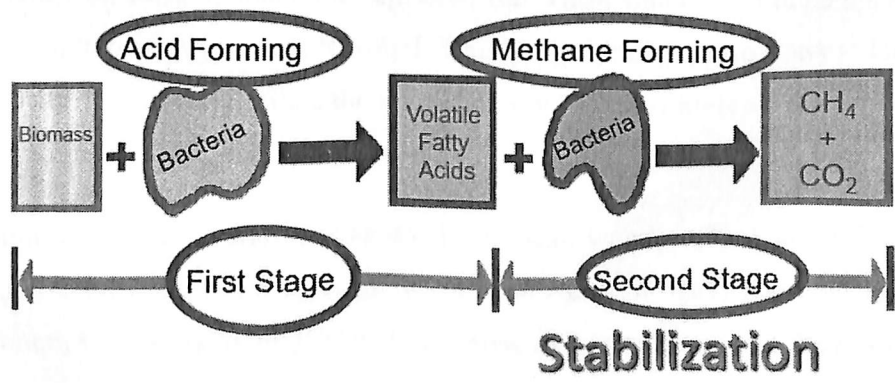


Fig 3: Simplified diagram of Anaerobic digestion process

There are many factors which affect the performance of anaerobic digestion process, such as reactor design, feedstock characteristics and operational conditions. But main important factor is organic loading rate (OLR), because it indicates the amount of volatile solids which is fed to the digester. These volatile solids represents the part of organic material which can be digested and remaining portion is the fixed solids, which are non- biodegradable.

Even though, it is one of the cost effective process to produce the Bio-gas, but it has many disadvantages. First of all, this process takes 30 to 40 days to give the yield of bio-gas of 50% containing around 60% of methane.

#### 1.4 Bio-oil

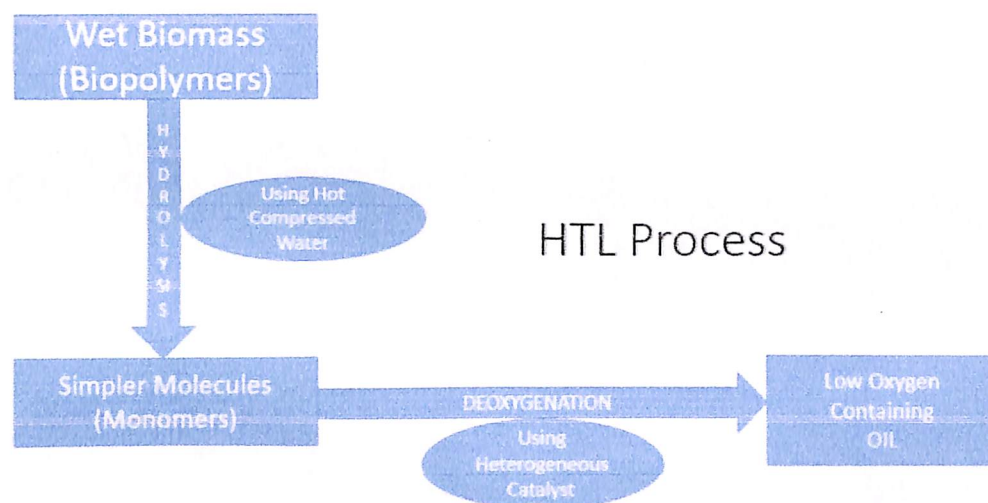
Bio-oil a potential substitute for gasoline and diesel after upgradation is produced from wide range of biomass employing thermochemical conversions namely pyrolysis [10, 11], hydrolysis [12] and hydrous pyrolysis or hydrothermal liquefaction (HTL) [13]. Among them, HTL has generated significant interest as it has several advantages over other thermochemical conversions [14], particularly ability to convert wet biomass and is regarded as mimic of natural process of formation of petroleum [15] but taking only hours to minutes unlike natural process taking millennium.

According to the recent report of Central Pollution Control Board (CPCB), India produces around 61754 MLD of wastewater out of which, the treating capacity is only around 22963 MLD, which results in discharge of untreated waste water into environment and thus affecting it. The current wastewater treatment facilities in India focus only on waste reduction except few. But waste water has a huge potential to be converted into energy such as Bio-fuel. Thus conversion of waste water to biofuels that can partly or wholly substitute the petroleum derived auto fuels attracts great attention and becomes an important area of research.

Existing energy generation processes from waste water such as anaerobic digestion could convert organic waste in the waste water into bio-gas. The constrains are the maximum % conversion of 50% and only 60% of it is methane and the rest to CO<sub>2</sub> and the process takes around 30 days, necessitating huge treatment plant. So there has to be a technology that can efficiently convert the waste into bio-oil at shorter time interval.



The Thermochemical Conversion technologies are efficient in converting the waste matter into Bio-oil at higher temperatures at shorter duration, such as Pyrolysis, hydrolysis and Hydrothermal Liquefaction. In Pyrolysis and hydrolysis, biomass is to be pretreated to reduce the water content less than 10% and hence unsuitable for waste water conversion to bio-oil. Secondly they use higher temperatures making the process energy intensive. Hydrothermal Liquefaction on the other hand uses sub critical water employing temperatures of 200 to 300 °C which has low dielectric



**Fig 4: Hydrothermal Liquefaction Process**

constant and high dissociation constant hence has high solubility for biomass and provides  $H^+$  and  $OH^-$  that helps to catalyze the hydrolysis of polysaccharides, fats and proteins into sugars, fatty acids and amino acids which undergoes deoxygenation in the presence of reducing gas and catalyst to give high yield of low oxygen containing bio-oil.

Use of catalyst, both heterogeneous and homogeneous in HTL process has been one of the impressive breakthroughs in the catalysis realm. The most promising one is heterogeneous catalyst, because it increases the bio-oil yield, but at the same time it also can be recovered and reused in the process. If the catalyst is having the pores of larger sizes, then it is easier for the bulky biopolymers in the waste water to reach the active sites of catalyst.

So in this project, the aluminum hierarchical zeolite and iron, cobalt substituted hierarchical zeolite will be synthesized and evaluated for HTL of synthetic waste water.

## 2.OBJECTIVES

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- Direct synthesis of Al, Fe, Co, Fe-Co Hierarchical Zeolite catalyst.
- Characterization using XRD, Surface area.
- Catalytic evaluation for hydrothermal liquefaction of synthetic waste-water into bio-oil.

### 3.Literature Survey

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In early 1920s, there was a concept of using hot water and alkali catalyst to produce bio-oil from bio-mass. During 1970s, Pittsburg Energy Research Center did demonstrate continuous scale High pressure HTL unit (at a scale of 100 kg/hr). Later in 1980s, Shell Oil Development, developed HTU® technology in Netherland. Currently, Pacific National North West Laboratory (PNNL), USA is working on commercialization of Hydrothermal liquefaction of various biomass to bio-oil, having the Bio-oil of least oxygen content at lesser price. [16]

PNNL in USA has developed a small scale Hydrothermal Liquefaction unit to study important parameters such as temperature, pressure, biomass loading, and type of catalyst used. Apart from that, they are also working on the optimization of the HTL bio-oil yield and feed Sludge content. The yield of Bio-oil reported by PNNL is around 40.2 % (dry ash free basis) using the feedstock containing 12% solids. [17]

Many researchers both in academia and research institution, are working towards the maximization of Bio-oil with lesser oxygen content, which is obtained from HTL. *Yunhua et al* has studied the bio-oil production from woody biomass as a feedstock by HTL, the feedstock containing the slurry of 15% of woody biomass has given the oil yield of 30 % (dry ash free basis). There is also a process modification suggested by the author, i.e the aqueous phase ,containing rich organics, can be send to anaerobic digestion to convert rich organics into valuable CH<sub>4</sub> and CO<sub>2</sub> [16].*Eduardo et al* reported the yield of bio-oil as 44.4% (dry ash free basis) by using the feedstock as domestic sewage from high-rate ponds. The solid concentration in the slurry feedstock was 16% of sewage. The author also studied effect of reaction time and temperature on the Bio-oil yield. The maximum bio-oil yield of 44.4% (dry ash free basis) at 300°C is achieved at a reaction time of 45 minutes [18]. Same kind of work is done by *Donghai Xu et at*, by taking the sewage sludge as a feed stock. Author studied the effect of temperature on the product yields (including gas, bio-oil, aqueous phase and solid residue) [19].

In all the temperatures, the yield of solid residue is much more as compared to other products. As reported by *Suzanne Anouti et al*, bio-oil from HTL is superior than other liquid fuel obtained from thermo-chemical conversion processes such as pyrolysis. This is because, the HTL Bio-oil has higher heating value of  $35.5 \text{ MJ kg}^{-1}$  and the oxygen content ranging from 15-20%, which is ideal for engine, because it is one of the factor which can prevent the engine from knocking [20]. *Linxi Yang et al* used spent coffee grounds as a feedstock in HTL process. In this process nitrogen is introduced as process gas as well as for pressuring the reactor, which has significantly increased the bio-oil yield by 47.3 % (ash free basis). According to the literature survey on non-catalytic Hydrothermal Liquefaction, this is highest yield of bio-oil reported by this author [21].

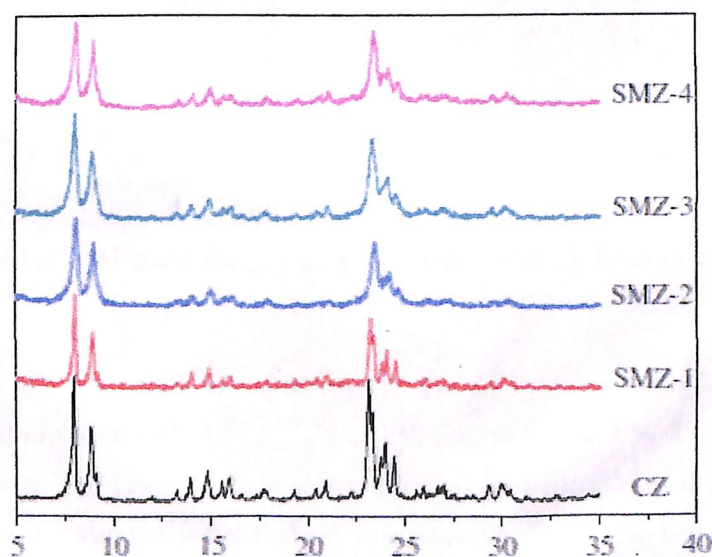
The use of homogeneous as well as heterogeneous catalyst has helped to maximize the bio-oil yield to a certain extent. *R Singh et al* used KOH as a homogeneous catalyst in the HTL of agricultural and forest biomass residue. According to the results reported by author, the time taken to reach 86% conversion is 15 min, which is much more lesser as compared to non-catalytic HTL and the maximum bio-oil yield was obtained 36 wt. % [22]. *Hwang et al* carried out Hydrothermal Liquefaction using Mongolian oak as a feedstock with  $\text{K}_2\text{CO}_3$  as a catalyst. The oil yield was around 27.7 wt% with the suspension of hydrochar [23]. *Ulf et al* studied the HTL using the feedstock as sugarcane bagasse and formate and water as catalyst to produce Bio-oil. The heavy oil, which was obtained from HTL having the oxygen content 20-30 wt% [24]. *Karagoz S et al* carried out HTL using Rb and Cs carbonates as catalyst to produce bio-oil from woody Bio-mass. The Solids content decreased with increase in Bio-oil content [25]. Despite the higher conversion showed by homogenous catalyst, the yield of bio-oil is very less with more oxygen content on it Use of heterogeneous catalyst to some extent has solved this problem. Recently reported by *Govindasamy et al*, by using Fe-MCM-41 and Co-MCM-41 as heterogeneous catalyst, the maximum bio-oil yield was reported around 57.6 wt.% containing very less oxygen around 10.8%. Despite the maximum oil yield exhibited by Fe and Co heterogeneous catalyst, there is an issue in the recovering the catalyst, because the oxides of Fe and Co needs a stable support in the catalyst, which MCM-41 failed to show [26]. *Tekin et al* studied the Hydrothermal Liquefaction of beech wood using calcium borate mineral as a catalyst, the oil yield was 41% with the oxygen content of 33.6%. [27] *Sun et al* reported the bio-oil yield of 36% containing the oxygen content of 19.4% by Hydrothermal Liquefaction of

Paulownia wood using Powdered Fe as the catalyst [28]. *Yan et al* reported the Catalytic Hydrothermal liquefaction of sugarcane bagasse using NaOH and ZSM-5 as a catalyst. Use of NaOH reduced the acids and furfural contents in the Bio-oil and use of ZSM-5 improved the fuel properties and reduced the oxygen and acidic contents of the Bio-Oil [29]. *Cheng et al* reported that the Hydrothermal Liquefaction of pine dust using Nickel substituted H-ZSM 5 as catalyst, yielded bio-oil with less oxygen content and more hydrocarbon content [30]. *Carlo Perego et al* suggested that, the normal zeolites cannot be readily used with the biomass because, firstly the normal zeolites have the pore diameter around half a nanometer, secondly the biomass consists of bulky polymers such as cellulose, hemicellulose, starch, lignin and proteins, has a difficulty in reaching the catalyst active sites, thus by hindering the mass transfer [31]. The Hierarchical Zeolite (like Hierarchical-ZSM-5), which is high in Silica content and has both microporous and mesoporous structure can provide the stable support to the Fe and Co and can be ideally used for hydrothermal liquefaction.

The several authors have studied the various methods to the synthesize Hierarchical ZSM-5. *L Meng et al* studied the direct synthesis of Hierarchical ZSM-5 using Ludox HS-40 as Silica source and CTAB (cetyltrimethylammonium) hydroxide as a structural directing agent and mesoporegen and Aluminum Hydroxide as an aluminum source. The author also studied the mechanism of Hierarchical ZSM-5 formation in the presence of Potassium Hydroxide and CTAB (cetyltrimethylammonium) hydroxide [32]. *D Nandan et al* studied the direct synthesis of Hierarchical ZSM-5 using organic structural directing agent as Tetrapropylammonium bromide (TPABr) and Silica source as Tetraethyl orthosilicate (TEOS) and Aluminum source as Aluminum nitrate. The author also studied the effect of porosity of the zeolite samples on using low cost template precursor which is glucose [33]. *G Song et al* used Organosiloxane-polyether amine (OPA) as a mesoporegen to synthesize hierarchical ZSM-5 by using Tetrapropylammonium bromide (TPABr) as organic structural directing agent and Tetraethyl orthosilicate (TEOS) as silica source and Sodium Aluminate as aluminum source. The synthesis was done using conventional hydrothermal crystallization method. The Hierarchical ZSM-5 samples showed super mesoporousity and great microporousity by using OPA as a mesoporegen [34]. In another publication, *G Song et al* used soft template to synthesize hierarchical ZSM-5 by using same organic structural directing agent, aluminum source and silica source as mentioned above. The

author also carried out the catalytic evaluation of alkylation reactions between benzene and benzylalcohol and thermal cracking reactions of Low Density Polyethylene (LDPE) and reported that Hierarchical ZSM-5 showed excellent selectivity towards the bulky molecules [35]. *Y Wang et al* studied the synthesis of hierarchical ZSM-5 using solid state crystallization method to eliminate the use of meso-template material. For the synthesis, Tetraethyl orthosilicate (TEOS) as silica source, Sodium Aluminate as aluminum source and Tetra propyl ammonium hydroxide (TPAOH) as organic structural directing agent is used. The performance of hierarchical ZSM-5 was evaluated by carrying out lignin depolymerization with ethanol in its super critical state. The results showed excellent catalytic performance, because of the penetration of bulky molecules on to the catalyst surface. [36]

*As the wastewater generation is one of the primary concern now a days, there are few authors who has worked on the HTL of wastewater to produce bio-oil [18] [19]. But, till now no one has reported on the HTL of domestic waste water using Hierarchical Zeolite incorporated with Co and Fe to give low oxygen containing bio-oil, which has a potential in solving the problem of fuel crisis (by giving higher oil yield) as well as for wastewater generation (value generation from waste).*



**Fig 5:** XRD of Hierarchical ZSM-5 as reported by (*Song et al*) [34]

## 4. Materials and Methods

### 4.1 Synthesis of Hierarchical Zeolite: -

Sodium Aluminate, Ludox HS -40 and aq. TEAOH (35wt%) of Sigma Aldrich make were used as source of Aluminum, Silicon and Organic Structure Directing agent (OSDA) respectively.

The list of hierarchical zeolites prepared are presented in the Table 1

Calculated quantity of Sodium Aluminate, Ludox HS-40, TEAOH (35wt%) and distilled water were mixed to yield the gel of composition  $x \text{Na}_2\text{O} \cdot x \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 0.1539 \text{TEAOH} \cdot 13.00 \text{H}_2\text{O}$  ( $x = 0.0248, 0.0167$  and  $0.0125$  having  $\text{Si}/\text{Al} = 40, 60, 80$  respectively). The gel was transferred to Teflon lined Stainless Steel Autoclave of



Fig 6: Gel Formation of Al Hierarchical Zeolite



Fig 7: -300 ml Teflon Lined Autoclave

capacity 300 ml. The autoclave was kept in the air oven maintained at  $175^{\circ}\text{C}$  for different crystallization time Viz 2, 3, 4, 5 and 6 days (S.No 1 to 5 of Table 1). To study the effect of crystallization temperature, crystallization of the same gel compositions were also carried out at  $165^{\circ}\text{C}$  for 3 and 5 days (S.No 6 to 13 of Table 1). The samples were filtered from mother liquor using vacuum filtration. The filter cake was dried in hot air oven at  $120^{\circ}\text{C}$  for 12 hours. Then the sample is calcined for 6 hours for  $550^{\circ}\text{C}$ .





**Fig 8:** Al Hierarchical Zeolite

Isomorphic substitution of Fe, Co, Fe-Co of hierarchical zeolite were carried out using the above procedure by replacing Sodium Aluminate with Sodium Hydroxide, Ferric Nitrate and /or Cobaltous Chloride for the gel of Si/M=40 (where M=Fe, Co or Fe-Co) at 175°C for 3 days (S.No 14 to 16 of Table 1).



**Fig 9:** Gel Formation of Fe-Co



**Fig 10:** -Hierarchical Fe-Co Zeolite



**Fig 11:** Filtration of solid from mother liquor during the synthesis of Hierarchical-Fe-Co

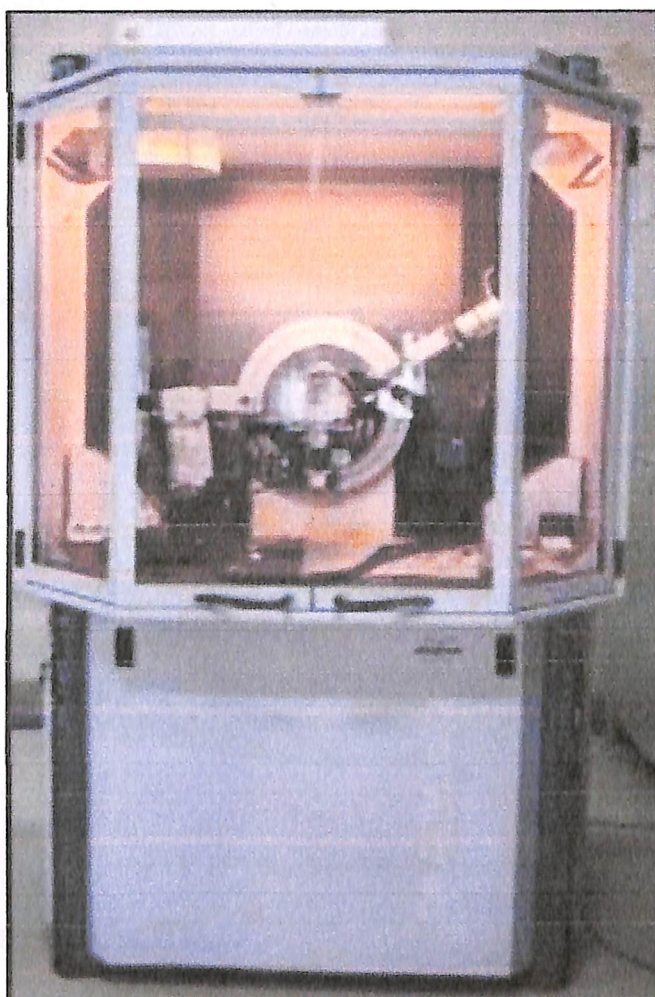
S. No	[Starting gel mol Si/Al] ] [Crystallization time in days] [Crystallization temperature in °C]	Sample Code
1	[40][2][175]	AlHZ1
2	[40][3][175]	AlHZ2
3	[40][4][175]	AlHZ3
4	[40][5][175]	AlHZ4
5	[40][6][175]	AlHZ5
6	[60][2][175]	AlHZ6
7	[60][3][175]	AlHZ7
8	[60][5][175]	AlHZ8
9	[80][2][175]	AlHZ9
10	[80][3][175]	AlHZ10
11	[80][5][175]	AlHZ11
12	[40][3][160]	AlHZ12
13	[40][5][160]	AlHZ13
<b>Isomorphically substituted Hierarchical Zeolites</b>		
S.No	[Starting gel mol Si/M] ] [Crystallization time in days] [Crystallization temperature in °C]	Sample Code
14	[40][3][175]	FeHZ14
15	[40][3][175]	CoHZ15
16	[40][3][175]	FeCoHZi6

**Table 1:** List of Hierarchical Zeolites prepared

## **4.2 Characterization: -**

### **4.2.1 X-Ray Diffraction: -**

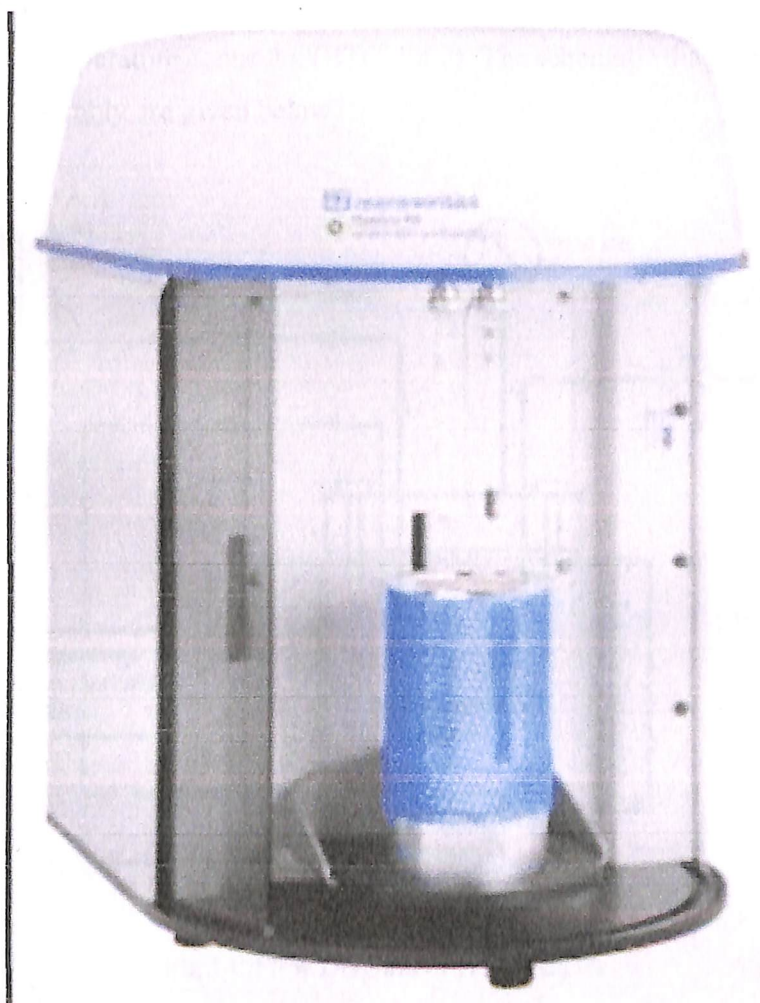
Approximately 0.5 g of catalyst sample initially grounded into fine powder, and then loaded into the sample holder. The XRD was recorded with Bruker D8 Advance diffractometer equipped with a crystallography open database (REV89244 2013.10.11), using nickel-filtered Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The  $2\theta$  scanning range was from  $5^\circ$  to  $60^\circ$ . The scanning speed was 0.1 sec/step.



**Fig 12: -XRD Instrument**

#### 4.2.2 BET Surface area: -

Approximately 0.5 g of catalyst sample is degassed at 200°C for 3 hours prior to measurement of surface area. The Surface area of a sample was analyzed at liquid nitrogen temperature using Micromeritics ASAP-2020 with built-in BJH algorithm software. The pore volume and pore size distribution were determined using t-plot and built in BJH algorithm analysis.



**Fig 13: BET Surface Area Instrument**

#### 4.3 Catalytic Evaluation for HTL: -

##### 4.3.1 Preparation of Synthetic Waste Water: -

8.25 gm of starch (Potato Starch, Molychem), 4.5 gm casein (Himedia), 2.25gm of soya oil (Goldwin) and 85 gm of distilled water was stirred together to get 100 g of synthetic

waste water containing 15% solids comprised of 55% carbohydrates, 30% protein and 15% fat.

#### 4.3.2 Hydrothermal Liquefaction of Synthetic Waste Water: -

The hydrothermal liquefaction of synthetic wastewater was carried out in stainless steel high-pressure reactor (BR 100 Berghof) of volume 170 ml with a magnetic stirrer equipped with Temperature controller (BTC-3000). The schematic diagram and picture of the reactor assembly are given below.

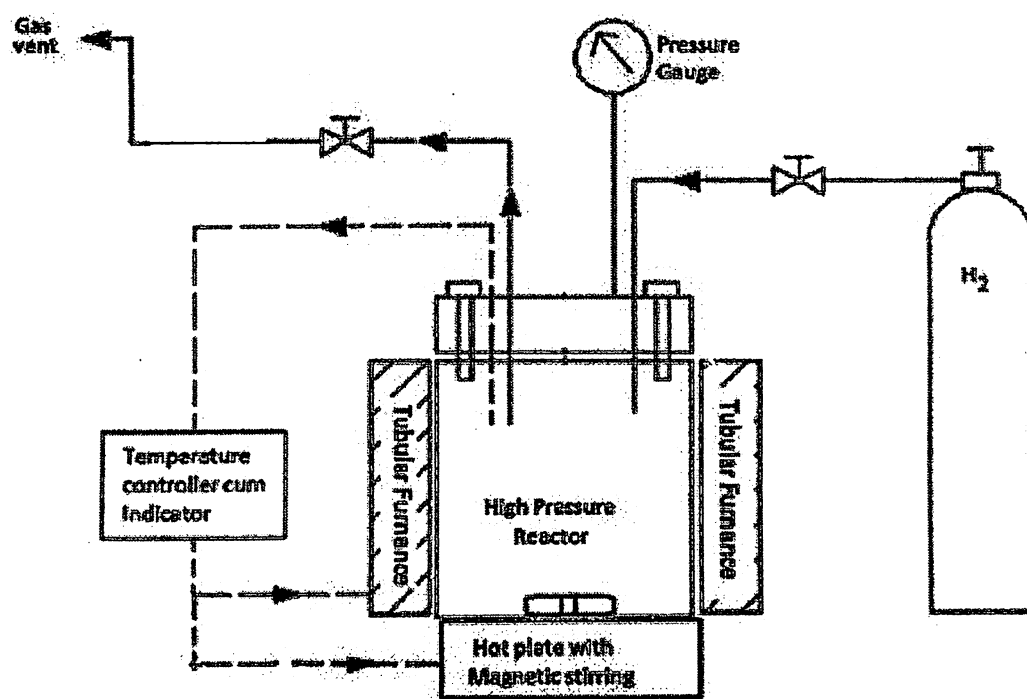


Fig 14: Flow Diagram of HTL Reactor

In the typical reaction run, 70 g of above mentioned synthetic waste water was transferred into the reactor and 0.5 g of catalyst was also added. The reactor was purged and pressurized with hydrogen gas to an initial pressure of 45 bar, and then sealed. Reactants were stirred by magnetic stirring at 1400 rpm. Then the reactor was heated to the reaction temperature of 200°C and maintained for 120 min. After the reaction, the reactor was cooled down to ambient temperature. The gaseous products were vented

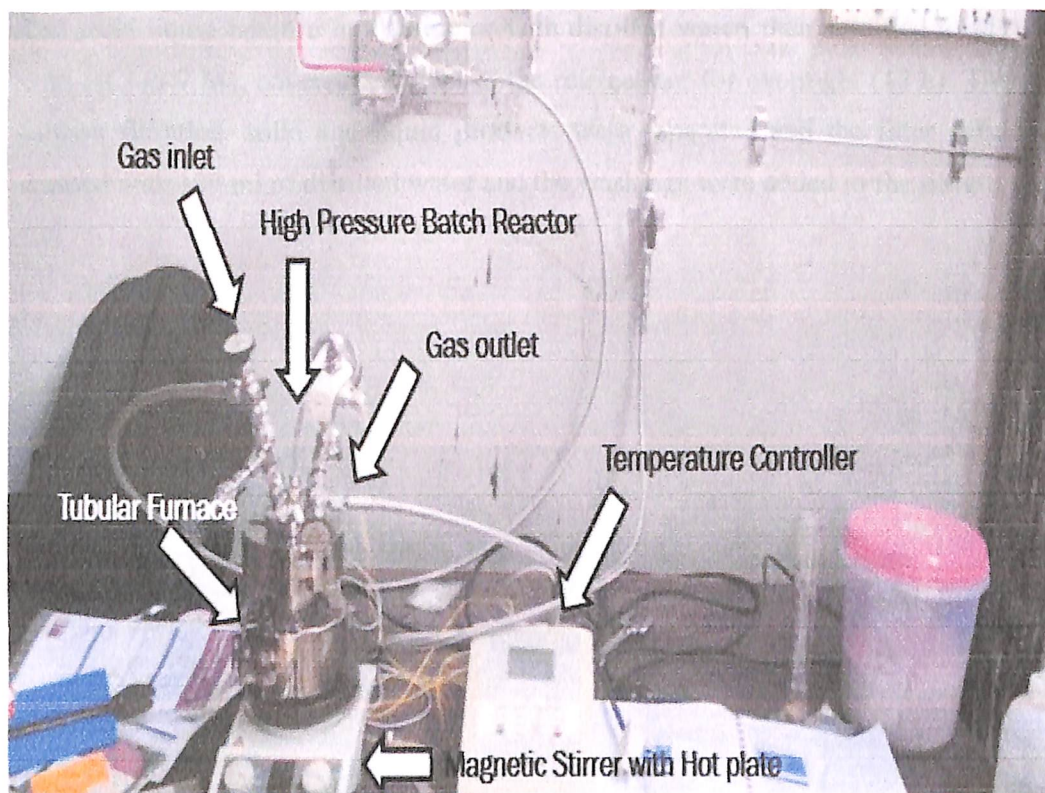


Fig 15: HTL Reactor Assembly

out. Then the remaining solid-liquid mixture was subjected to product separation, by following the procedure reported by *Karagoz et al.* [14].

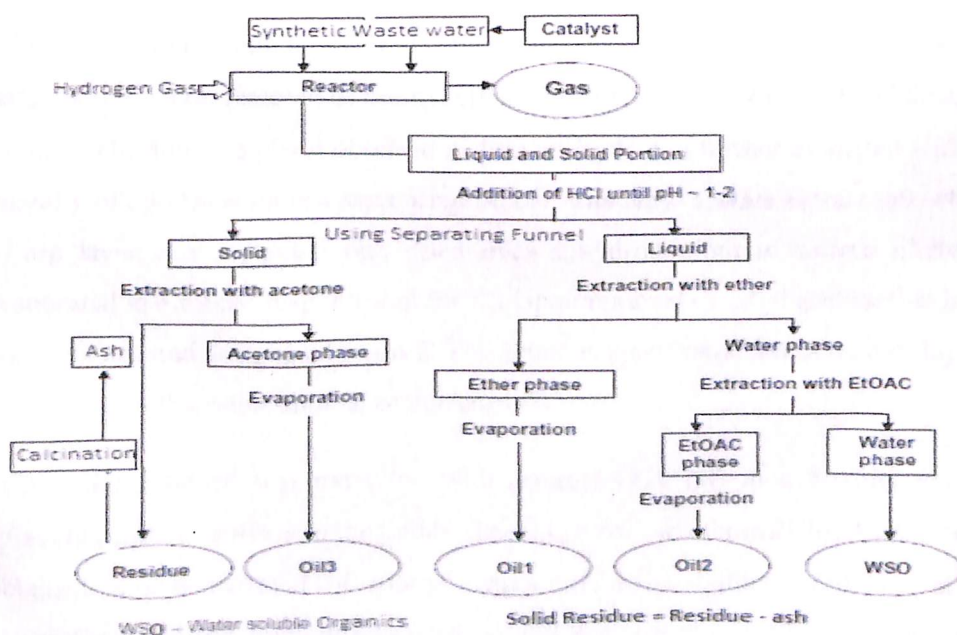
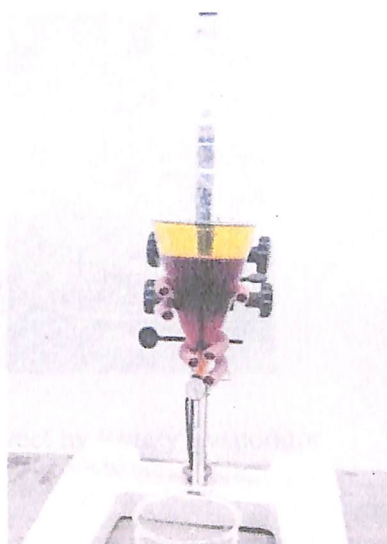


Fig 16: -Schematic diagram for HTL product separation (*Karagoz et al*) [14]

The solid-liquid mixture in the reactor with distilled water, then acidified to pH 1–2 with HCl (1.7 M), covered and kept in the refrigerator for overnight (12 h). Then by suction filtration, solid and liquid products were separated and the filter cake was washed with 100 ml of distilled water and the washings were added to the filtrate.



**Fig 17:** -Separation of Solids and Liquid using vacuum Filtration



**Fig 18:** -Separation of aqueous phase and organic phase in separating funnel

The liquid filtrate was extracted with equal quantity of diethyl ether in a separating funnel. The ethereal extract thus obtained as top layer was separated out and dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator at room temperature. Upon removal of diethyl ether, this fraction was weighed and designated as oil 1. The aqueous phase obtained as bottom layer was further extracted with equal quantity of ethyl acetate in a separating funnel. The ethyl acetate extract thus obtained as top layer was separated out, dried over anhydrous sodium sulfate filtered and evaporated in a rotary evaporator at 50 °C. Upon removal of ethyl acetate this fraction was weighed and designated as oil 2. The aqueous phase obtained as bottom layer was designated as the water-soluble oxygenates (WSO).

Filter cake obtained was extracted with acetone (150 ml) in a Soxhlet extraction apparatus until the solvent in the thimble became colorless (about 20 h). Acetone extract obtained was evaporated in rotary evaporator under reduced pressure at room temperature and this fraction was weighed and designated as oil 3. Acetone insoluble

fraction was dried at 105 °C and then weighed to get the amount of Residue. As the Residue included the catalyst, it was calcined at 500°C, cooled and weighed to get the weight of Ash. The difference between the weight of Residue and Ash was designated as Solid residue (biochar).



**Fig 19:** -Removal of solvent from extract by Rotary Evaporator



**Fig 20:** -Extracting Oil 3 from solids using acetone in Soxhlet Apparatus



### 4.3.3 Calculations

Yield of different oils, Solid Residue, Conversion and % Yield of Total Oil were calculated as per the following equations.

To calculate % Yield of the HTL products,

- % Yield of Oil 1, Oil 2, Oil 3 and Solid residue (SR)

$$= \frac{\text{Yield of Oil 1,2,3 or Solid residue}}{\text{Weight of initial Solids in Synthetic wastewater}}$$

- % Conversion = 100 - % yield of Solid residue

- % Yield of Total Oil =  $\frac{\text{Yield of Oil 1} + \text{Yield of Oil 2} + \text{Yield of Oil 3}}{\text{Weight of Solids in Synthetic wastewater}}$

Yield of Gas & WSO was calculated on the basis of material balance using the following equation;

- % Gas & WSO Yield

$$= 100 - \% \text{Yield of (Oil 1 + Oil 2 + Oil 3 + SR)}$$

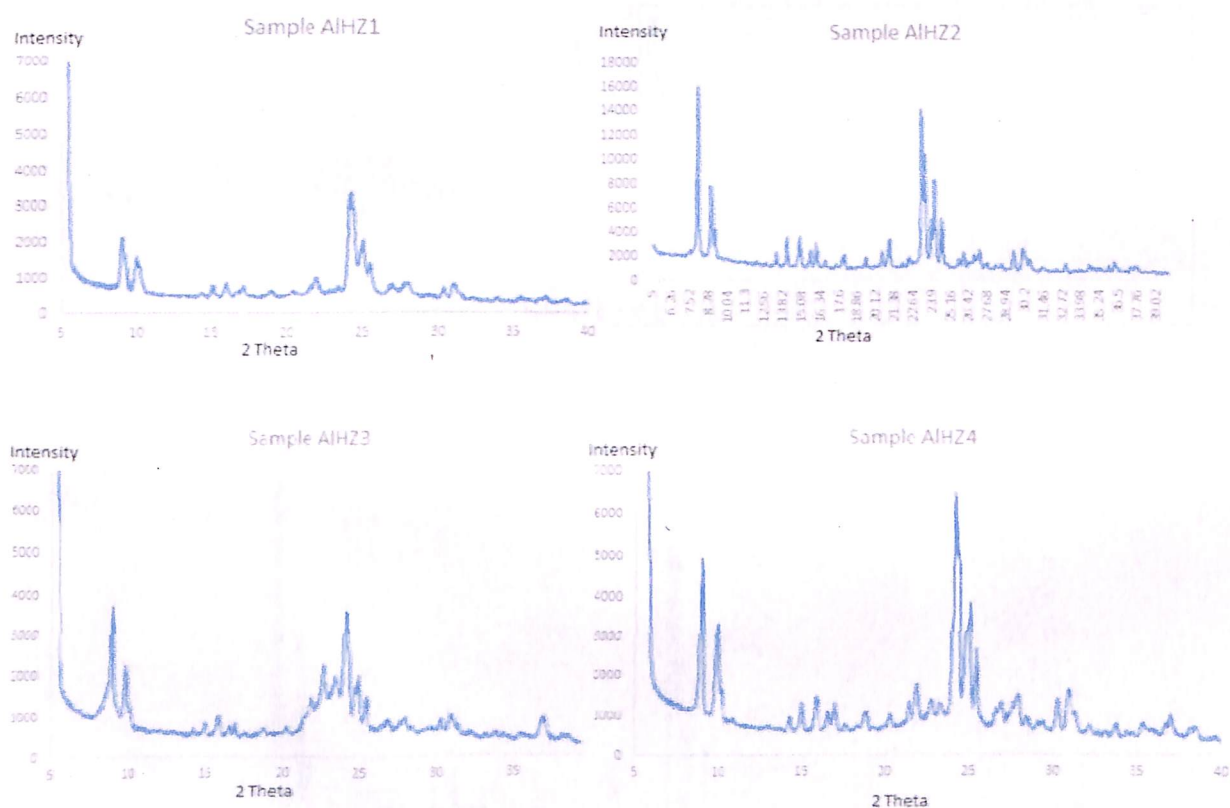
## 5. Results and Discussions

### 5.1 XRD Characterization

XRD pattern of the hierarchical zeolites are presented in the Fig 21-23

#### 5.1.1 Effect of Crystallization Time on the crystallization of starting gel Si/Al =40

As the crystallization time was increased from 2 to 3 days, crystallinity increased and with further increase to 4 and 5 days, crystallinity decreased indicating that optimum crystallization time for the gel of Si/Al ratio of 40 is 3 days. (Fig 21.)



**Fig 21:** -Effect of crystallization time on the crystallinity of starting gel Si/Al=40

### 5.1.2 Effect of Crystallization Time on the crystallization of starting gel Si/Al=60

For the gel of starting Si/Al ratio of 60, as the crystallization time was increased from 3 to 5 days, crystallinity increased. (Fig.22)

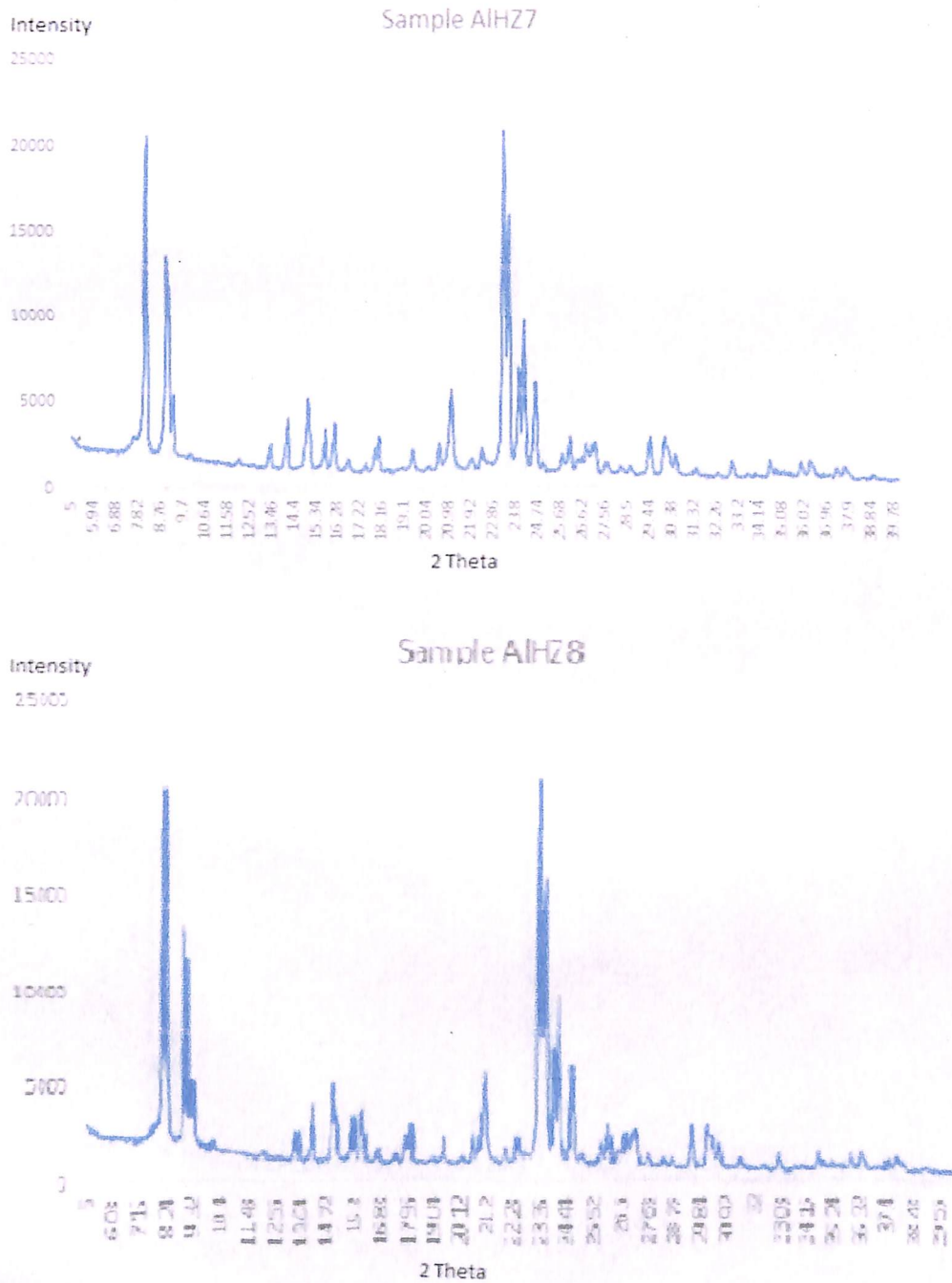


Fig 22: -Effect of crystallization time on the crystallinity of starting gel Si/Al=60

### 5.1.3 Effect of Crystallization Time on the crystallization of starting gel Si/Al=80

For the gel of starting Si/Al ratio of 80, as the crystallization time was increased from 3 to 5 days, crystallinity decreased (Fig.23).

From these results, it can be concluded that optimum crystallization depends on the starting gel Si/Al ratio.

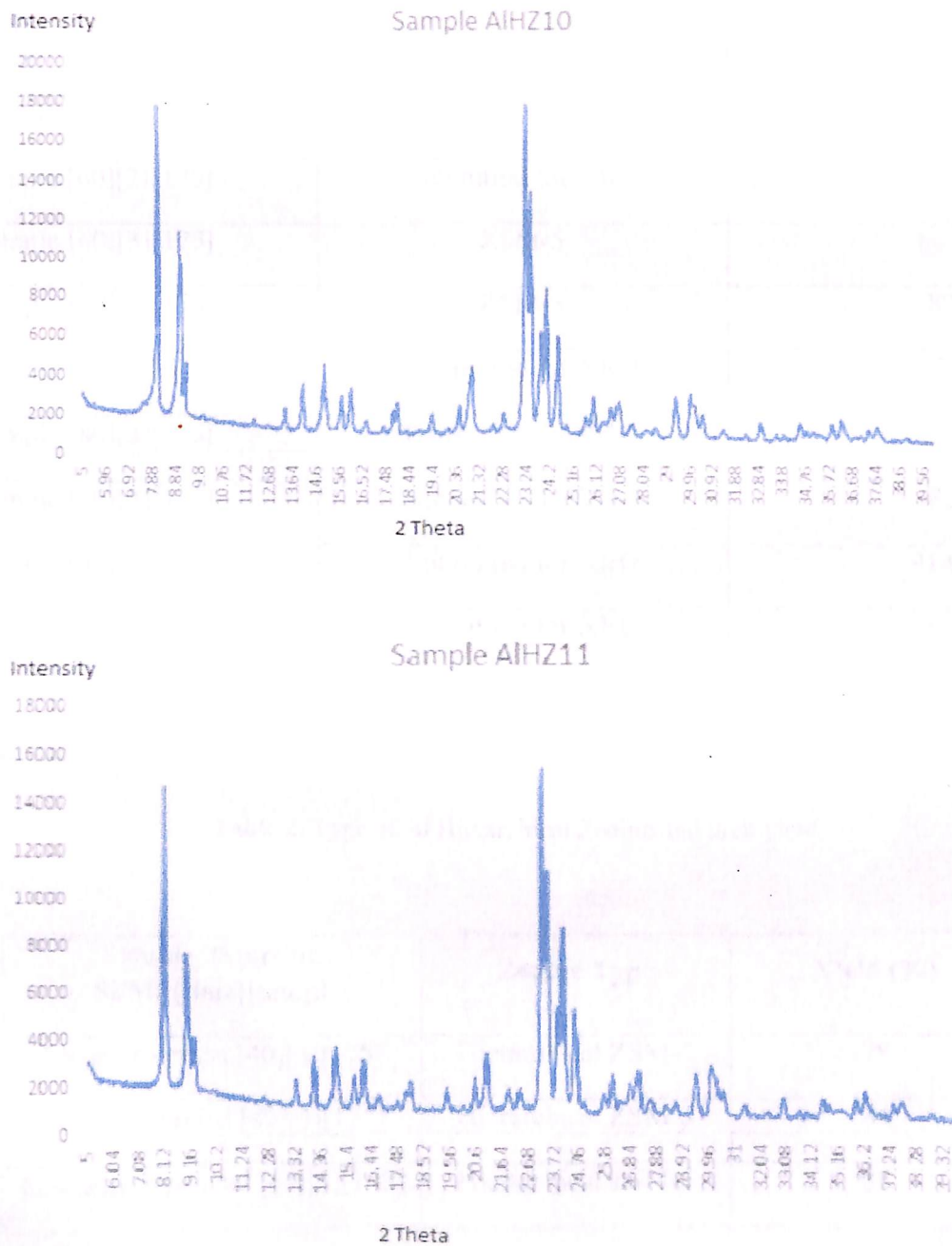


Fig 23: -Effect of crystallization time on the crystallinity of starting gel Si/Al=80

Sample [Starting Si/Al][time][temp]	Zeolite Type	Yield (%)
Sample [40][2][175]	ZSM-5	68
Sample [40][3][175]	Hierarchical ZSM-5	71
Sample [40][4][175]	ZSM-5 with impurity	68
Sample [40][5][175]	ZSM-5	58
Sample [40][6][175]	Submitted for XRD	80
Sample [60][2][175]	Submitted for XRD	66
Sample [60][3][175]	ZSM-5	86.8
Sample [60][5][175]	ZSM-5	82
Sample [80][2][175]	Submitted for XRD	77.6
Sample [80][3][175]	Hierarchical ZSM-5	82.4
Sample [80][5][175]	Hierarchical ZSM-5	85
Sample [40][3][165]	Submitted for XRD	91.94
Sample [40][5][165]	Submitted for XRD	78.01

**Table 2:** Type of Al Hierarchical Zeolite and their yield

Sample [Starting Si/Ml][time][temp]	Zeolite Type	Yield (%)
Fe-incorporated [40][3][175]	Hierarchical ZSM-5	79
Co-incorporated [40][3][175]	Hierarchical ZSM-5	84
Fe-Co incorporated [40][3][175]	Hierarchical ZSM-5	88

**Table 3:** Type of zeolite and yield of Fe and Co incorporated Hierarchical Zeolite.

From the Table 2, it can be found that the gels having the starting gel Si/Al of 40 and 60, the yield increased from 2 to 3 days and then decreased with further increase to 4 and 5 days as in the case of crystallinity. Whereas for the gel having the starting gel Si/Al of 80, yield increased with increase in crystallization time from 3 to 5 days.

From the Table 3, it is evident that the yield of Fe and Co substituted hierarchical ZSM-5 is higher than Al hierarchical ZSM 5 for the same starting Si/M ratio of 40 for 3 days at 175°C.

### 5.2 Surface Area Characterization

The adsorption isotherm of hierarchical Al ZSM-5 obtained from gel of starting Si/Al ratio of 40 at 175°C for 3 days (AlHZ-2) is presented in Fig. 24. From the graph, it can be observed that it follows Type-II adsorption isotherm.

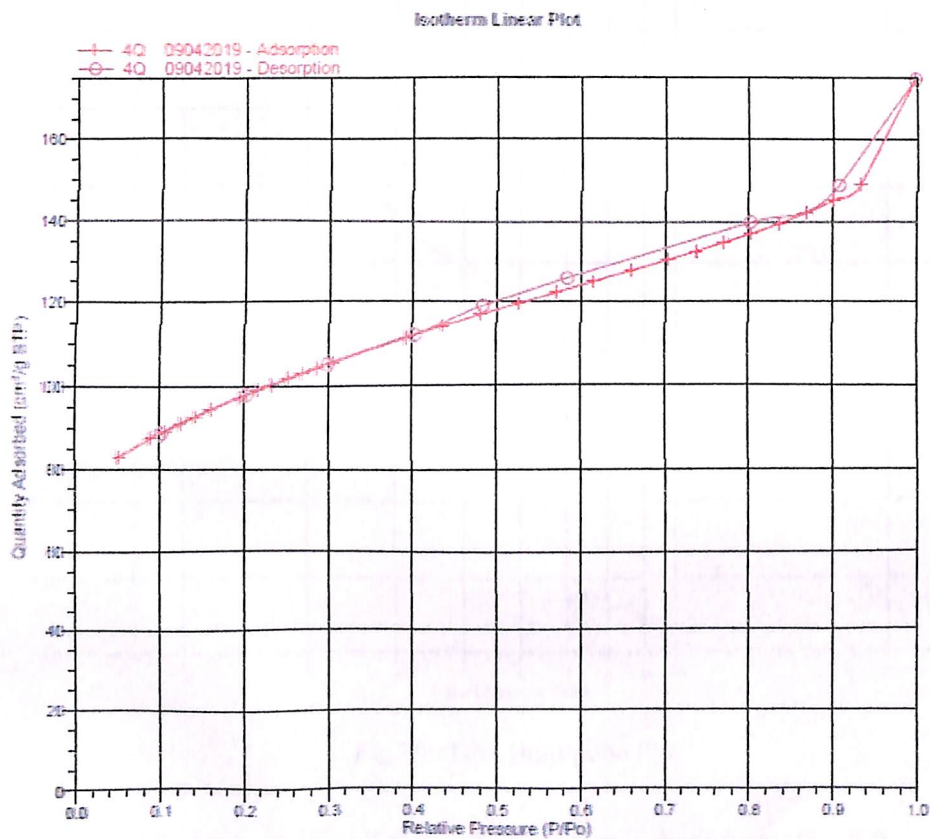
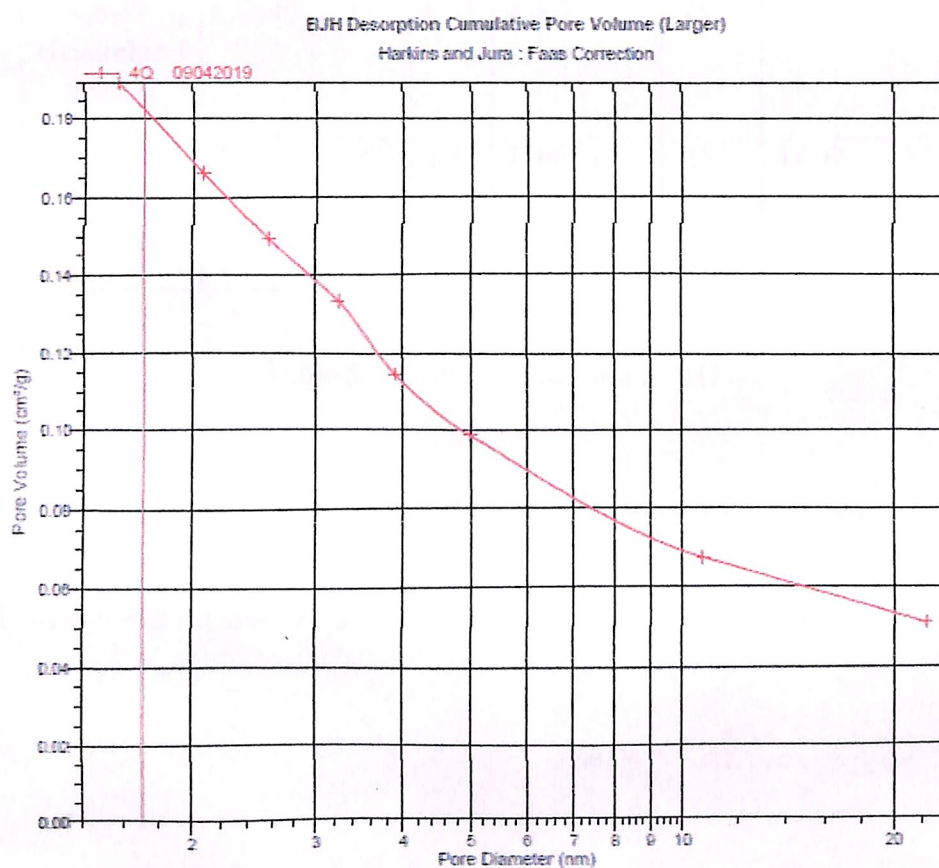


Fig 24: Adsorption Isotherm

Pore Diameter Range (nm)	Average Diameter (nm)	Incremental Pore Volume (cm <sup>3</sup> /g)	Cumulative Pore Volume (cm <sup>3</sup> /g)	Incremental Pore Area (m <sup>2</sup> /g)	Cumulative Pore Area (m <sup>2</sup> /g)
1430.1 - 22.2	22.4	0.051014	0.051014	9.097	9.097
22.2 - 10.7	12.6	0.016289	0.067303	5.169	14.266
10.7 - 5.0	5.8	0.031358	0.098662	21.532	35.798
5.0 - 3.9	4.3	0.016010	0.114672	15.002	50.801
3.9 - 3.2	3.5	0.018815	0.133487	21.625	72.426
3.2 - 2.6	2.8	0.015768	0.149255	22.450	94.876
2.6 - 2.1	2.2	0.017135	0.166390	30.484	125.360
2.1 - 1.6	1.7	0.023526	0.189917	54.396	179.755

**Table 4:** Table of BJH Desorption report



**Fig 25:** BJH Desorption Plot

The BET Surface area, Total, micro and mesopore volume of the Sample (AIHZ-2) are 321.0993 m<sup>2</sup>/g, 0.189917 cm<sup>3</sup>/g, 0.023526 cm<sup>3</sup>/g and 0.1664 cm<sup>3</sup>/g respectively (Table 4) and thus % mesoporosity is 87.7 indicating that the synthesized zeolite is hierarchical.

5.3 Results on Hydrothermal Liquefaction Studies: -

Run	Catalyst	Yield (g)				% Gas & WSO yield	%Total Oil Yield	% Conversion
		Oil 1 (g)	Oil 2 (g)	Oil 3 (g)	Solid Residue(g)			
1	Co-Fe Hierarchical ZSM-5	0.9640	2.66	4.91	2.058	5.9	75.8	81.71
2	Co Hierarchical ZSM-5	1.890	1.805	1.6	1.94	35	47.07	82.76

**Table 5:** Catalytic evaluation for HTL

From Table 5, it can be found that % Conversion obtained for synthetic waste water over Co Hierarchical ZSM-5 is 1% higher than over Co-Fe Hierarchical ZSM-5 but the %Total Oil Yield is lower by 28.7%. This lower yield may be either because higher % Gas & WSO Yield.



## 6. REFERENCES

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1. M. Balat and H. Balat, "Recent trends in global production and utilization of bio-ethanol fuel," *Applied Energy*, vol. 86, no. 11, pp. 2273–2282, 2009.
2. J. K. Saini, R. Saini, and L. Tewari, "Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments," *3 Biotech*, vol. 5, no. 4, pp. 337–353, 2014.
3. R. Gunn and P. K. Rahman, "Processing of Bioethanol from Lignocellulosic Biomass," *Advances in Biofeedstocks and Biofuels*, pp. 1–24, 2017.
4. Vohra Mustafa, Manwar Jagdish, Manmode Rahul, Padgilwar Satish, and Patil Sanjay. "Bioethanol production: Feedstock and current technologies", *Journal of Environmental Chemical Engineering*, vol. 2, p. 573–584, 2014
5. Banerjee S, Mudliar S, Sen R, Giri L, Satpute D, Chakrabarti T, and Pandey RA. "Commercializing lignocellulosic bioethanol: technology bottlenecks", *Biofuels, Bioproducts and Biorefining*, vol. 4, p. 77–93, 2010.
6. Dwivedi P, Alavalapati JRR, and Lal P. "Cellulosic ethanol production in the United States: conversion technologies, current production status, economics, and emerging developments", *Energy for Sustainable Development*, vol. 13, p. 174–182, 2006.
7. .T. Vasudevan, and M. Briggs, *Journal of Industrial Microbiology and Biotechnology*, Vol. 35, p. 421–430, 2008
8. L. T. Thanh, K. Okitsu, L. V. Boi, and Y. Maeda, "Catalytic Technologies for Biodiesel Fuel Production and Utilization of Glycerol: A Review," *Catalysts*, vol. 2, no. 1, pp. 191–222, 2012.
9. A. Kumari, P. Mahapatra, V. Garlapati, and R. Banerjee, "Enzymatic transesterification of Jatropha oil," *Biotechnology for Biofuels*, vol. 2, no. 1, p. 1, 2009.

10. D. Mohan, C. U. Pittman, and P. H. Steele, "Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review," *Energy & Fuels*, vol. 20, no. 3, pp. 848–889, 2006.
11. D. Vamvuka, "Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes-An overview," *International Journal of Energy Research*, vol. 35, no. 10, pp. 835–862, 2011.
12. O. Onay, A. Gaines, O. Kockar, M. Adams, T. Tyagi, and C. Snape, "Comparison of the generation of oil by the extraction and the hydrolysis of biomass," *Fuel*, vol. 85, no. 3, pp. 382–392, 2006.
13. S. S. Toor, L. Rosendahl, and A. Rudolf, "Hydrothermal liquefaction of biomass: A review of subcritical water technologies," *Energy*, vol. 36, no. 5, pp. 2328–2342, 2011.
14. A. Gollakota, N. Kishore, and S. Gu, "A review on hydrothermal liquefaction of biomass," *Renewable and Sustainable Energy Reviews*, vol. 81, pp. 1378–1392, 2018.
15. M. D. Lewan, J. C. Winters, and J. H. McDonald, "Generation of Oil-Like Pyrolyzates from Organic-Rich Shales," *Science*, vol. 203, no. 4383, pp. 897–899, 1979.
16. Zhu, Yunhua, et al. "Techno-Economic Analysis of Liquid Fuel Production from Woody Biomass via Hydrothermal Liquefaction (HTL) and Upgrading." *Applied Energy*, vol. 129, 2014, pp. 384–394., doi: 10.1016/j.apenergy.2014.03.053.
17. LJ Snowden-Swan , JM Billing "Hydrothermal Liquefaction and Upgrading of Municipal Waste water Treatment Plant Sludge:A Preliminary Techno-Economic Analysis." *Pacific Northwest National Laboratory Report*. June (2016).

18. Couto, Eduardo Aguiar, et al. "Hydrothermal Liquefaction of Biomass Produced from Domestic Sewage Treatment in High-Rate Ponds." *Renewable Energy*, vol. 118, 2018, pp. 644–653., doi: 10.1016/j.renene.2017.11.041.
19. D. Xu, G. Lin, L. Liu, Y. Wang, Z. Jing, and S. Wang, "Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures," *Energy*, vol. 159, pp. 686–695, 2018.S.
20. Anouti, G. Haarlemmer, M. Déniel, and A. Roubaud, "Analysis of Physicochemical Properties of Bio-Oil from Hydrothermal Liquefaction of Blackcurrant Pomace," *Energy & Fuels*, vol. 30, no. 1, pp. 398–406, 2015.
21. L. Yang, L. Nazari, Z. Yuan, K. Corscadden, C. (C. Xu, and Q. (S. He, "Hydrothermal liquefaction of spent coffee grounds in water medium for bio-oil production," *Biomass and Bioenergy*, vol. 86, pp. 191–198, 2016.
22. R. Singh, A. Prakash, B. Balagurumurthy, R. Singh, S. Saran, and T. Bhaskar, "Hydrothermal liquefaction of agricultural and forest biomass residue: comparative study," *Journal of Material Cycles and Waste Management*, vol. 17, no. 3, pp. 442–452, 2014.
23. Hwang, H., Lee, J.H., Choi, I.-G., Choi, J.W. 2018," Comprehensive characterization of hydrothermal liquefaction products obtained from woody biomass under various alkali catalyst concentrations". *Environmen. Technol.* In press
24. U. Schuchardt and F. D. A. P. Matos, "Liquefaction of sugar cane bagasse with formate and water," *Fuel*, vol. 61, no. 2, pp. 106–110, 1982.
25. S. Karagöz, T. Bhaskar, A. Muto, and Y. Sakata, "Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass," *Fuel*, vol. 83, no. 17-18, pp. 2293–2299, 2004.

26. G. Govindasamy, R. Sharma, and S. Subramanian, "Studies on the effect of heterogeneous catalysts on the hydrothermal liquefaction of sugarcane bagasse to low-oxygen-containing bio-oil," *Biofuels*, pp. 1–11, 2018.
27. K. Tekin, S. Karagöz, and S. Bektaş, "Hydrothermal liquefaction of beech wood using a natural calcium borate mineral," *The Journal of Supercritical Fluids*, vol. 72, pp. 134–139, 2012.
28. Sun, Peiqin, Heng, Mingxing, Sun, Shaohui and Chen, Junwu, (2010), "Direct liquefaction of paulownia in hot compressed water: Influence of catalysts", *Energy*, **35**, issue 12, p. 5421-5429.
29. Yan, X., Ma, J., Wang, W., Zhao, Y., and Zhou, J. (2018). "The effect of different catalysts and process parameters on the chemical content of bio-oils from hydrothermal liquefaction of sugarcane bagasse," *BioRes.* 13(1), 997-1018.
30. Cheng S, Wei L, Alsowij M, et al. "Catalytic hydrothermal liquefaction (HTL) of biomass for bio-crude production using Ni/HZSM-5 catalysts." *AIMS Environ Sci.* 2017;4(3): 417–430
31. Perego, Carlo, et al. "Zeolite Materials for Biomass Conversion to Biofuel." *Energy & Fuels*, vol. 31, no. 8, 2017, pp. 7721–7733., doi: 10.1021/acs.energyfuels.7b01057.
32. L. Meng, B. Mezari, M. G. Goesten, and E. J. M. Hensen, "One-Step Synthesis of Hierarchical ZSM-5 Using Cetyltrimethylammonium as Mesopore and Structure-Directing Agent," *Chemistry of Materials*, vol. 29, no. 9, pp. 4091–4096, 2017.
33. D. Nandan, S. K. Saxena, and N. Viswanadham, "Synthesis of hierarchical ZSM-5 using glucose as a templating precursor," *J. Mater. Chem. A*, vol. 2, no. 4, pp. 1054–1059, 2014.

34. G. Song, W. Chen, P. Dang, Y. Wang, and F. Li, "Synthesis of an excellent MTP catalyst: hierarchical ZSM-5 zeolites with great mesoporosity," *Royal Society Open Science*, vol. 5, no. 12, p. 181691, 2018.
35. G. Song, W. Chen, P. Dang, S. Yang, Y. Zhang, Y. Wang, R. Xiao, R. Ma, and F. Li, "Synthesis and Characterization of Hierarchical ZSM-5 Zeolites with Outstanding Mesoporosity and Excellent Catalytic Properties," *Nanoscale Research Letters*, vol. 13, no. 1, 2018.
36. Y. Wang, J. Song, N. C. Baxter, G.-T. Kuo, and S. Wang, "Synthesis of hierarchical ZSM-5 zeolites by solid-state crystallization and their catalytic properties," *Journal of Catalysis*, vol. 349, pp. 53–65, 2017.
37. S. Karagoz, T. Bhaskar, A. Muto, and Y. Sakata, "Hydrothermal upgrading of biomass: Effect of KCO concentration and biomass/water ratio on products distribution," *Bioresource Technology*, vol. 97, no. 1, pp. 90–98, 2006

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1. INTRODUCTION Population and industrial growth have increased the demand for energy. World and India primary energy consumption were 13,511 and 753 million toe respectively in 2017 thus making India the third largest consumer next only to China and USA. The share of fossil fuels share of total primary energy consumption of the world continue to be over 80% resulted in CO<sub>2</sub> emission of 32.5 giga tons in the year 2017 alone and its cause of global warming is at alarming rate. The growth in automobiles have increased the consumption of petroleum derived fuels namely motor spirit and diesel resulting in fast depletion of petroleum and its cost escalation. The world proven petroleum reserve as per available 2017 statistics was 1.7 trillion barrels; annual consumption was 33.6 billion barrels and thus expected to last only for 50.8 years. To address the twin sustainability issues of long-term availability of fossil fuels and global warming, diversifying the energy basket and increasing the share of renewable energy is the only option. Among the options of renewable energy such as solar, wind, tidal, biofuels etc., the biofuels is of very important as they have potential to sustain two billion vehicles already on the road which cannot be scrapped for the want of fuels. Important categories of biofuels are bioethanol, biodiesel, biogas and biooil. 1.1 Bioethanol Among the biofuels, bioethanol a substitute for gasoline demands carbohydrates as biomass feedstock employing