Hydrogenation of Vegetable Oil over NiMo-S/γ-Al_2O_3, Pt/β-Zeolite & Pd/C Catalysts for Biodiesel Production

Master of Science Thesis

Innovative & Sustainable Chemical Engineering (MPISC)

Ali Akhlaq Mughal

Department of Chemical and Biological Engineering

Division of Applied Surface Chemistry

CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden, 2011

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Abstract

Rapid growth of energy market, demand for domestic / commercial applications of fuel and tough legislation on green house gases production has led to the concept of using renewable energy resources such as vegetable and animal fats.

This research was based on hydro-treatment of rapeseed oil over three different catalysts NiMo-S/Al_2O_3, Beta-Zeolite & Palladium with 5% activated carbon to study the effect of temperature, pressure profiles with extent of reactivity and yield for production of biodiesel since vegetable oil is one alternative for biofuels.

Transesterification is one commercial method but comes with high investment costs and other complications to produce typical type of fuel whereas hydro treatment process is alternate to replace transesterification.

During the thesis, appropriate operational conditions to get maximum efficiency of catalyst with higher yield of biodiesel were investigated by running number of experiments at constant H_2 pressure of 40 bar and over temperature range of 280 °C – 360 °C. The feed used was 20% rapeseed oil with 80% decane as solvent in batch reactor Autoclave by Parr Instruments.

Selectivity for C_{18}, CO and CO_2 were of interest when it comes to results by comparing three catalysts. High yield of C_{18} was observed with NiMo-S/Al_2O_3 as compared to Pd/C and Pt/β-Zeolite. This may be due to small pore size and less activity by catalysts.

The presence of C_{18} compounds or C_{17} was either absent or quite low in Pd/C and Pt/β-Zeolite due to low catalytic activity and more production of intermediate compound like stearaldehyde was found even at 360 °C. The selectivity of C_{18} was highest at 360 °C with NiMo-S following with high concerntration of C_{17} and low % of CO / CO_2 gases while giving out high conc. of Propane whereas in case of Pt/β-Zeolite, concerntration of CO & CO_2 was relatively high.

In conclusion to the studies carried out, more stress should be given on the kinetic mechanism evaluation. Also β-Zeolite with some good active agent than Pt can be of interest. One more thing which was observed to have great influence on reactivity and yield was the pore sizes on the catalyst surface which were really small in Pd/C & β-Zeolite. Materials with high pore sizes can play important role due to the pore diffusion as it will provide with large area of contact and longer time period for reaction occurring at and inside pores.

Preface

With this master thesis, I conclude my studies for Innovative & Sustainable Chemical Engineering Program at Chalmers University of Technology, Göteborg Sweden.

This thesis work was carried out at Applied Surface Chemistry, Chemical & Biological Engineering Department at CTH.

The examiner for the master thesis has been Associate Professor Börje S. Gevert. The experiments and analytical work has been performed under the supervision of Shanmugam Palamisamy.

Acknowledgements

Before anything else, I would start by paying my submission to Allah Almighty for giving me the strength and helping me out with HIS unlimited grace in all the hard times of my life.

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Ali A. Mughal

Göteborg, October’2011

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Chapter One - Introduction

Objective

The purpose of the research is focused on the selection of better catalyst on the basis of yield and efficiency and also to derive a better temperature range for the process. The three catalysts are compared on different temperatures with more prominent results for high cetane number between 300-360^{O}C giving C_{n-1} compounds in product.

Background

Presently, world is going towards the major energy crisis which was started during 1970s due to the fact that world needs more energy than can be produced only from fossil fuel resources. These fuels are never environment friendly and are natural gas, crude oil and coal etc. To fill in the economic and sustainable gap, biofuels can be one of the alternatives. The demand for other energy resources is increased due to diminishing of fossil fuels, climate change and increase of prices. Thus biofuels are important alternate source of energy. Some of the advantages of this technology are that they produce less emissions and green-house gases. Also they contain 10-45% oxygen which is more than in fossil fuels [1].

Before in the past many years ago, the energy demands of human society was met with normally biomass feeds which was later changed its coarse and started using the naturally occurring fuel by discovery of fossil fuels during 19th century. Nowadays since fossil fuels are vanishing rapidly due to large industrialization, there is a definite need of some alternate energy sources such as Solar, Wind and Bio etc. Since bio-fuels have the capacity of filling the gap in energy deficit on the availability of huge raw material, biodiesel is certainly of great importance in the coming year.

Biodiesel can be derived from renewable sources like vegetable oils on the basis of containing large organic carbon contents. Another advantage in using the bio-fuels is that they produce 95-98% less carbon emissions and 10-45% more oxygen contents so they are more sustainable for society. During the 20th century, biofuels have been produced by processes like trans-esterification and methyl fatty acid esters for which the term used is biodiesel [2].

Chapter Two – Literature Review

Raw Material

Although there are number of renewable raw materials available today for the production of bio-fuels/biodiesel but mostly the work and studies are based/carried out on natural oils and fats originating from vegetables & animal feed stocks.

Vegetable Oil

Veg. oil mostly contains tri-glycerols up to 98% with the presence of some fatty acids, di-glycerides & mono-glycerides. Fatty acid values vary between C_6-C_{24} having mostly C_{16}-C_{18} which are saturated or mono-saturated as well as sometimes poly-unsaturated nature [3, 4,5].

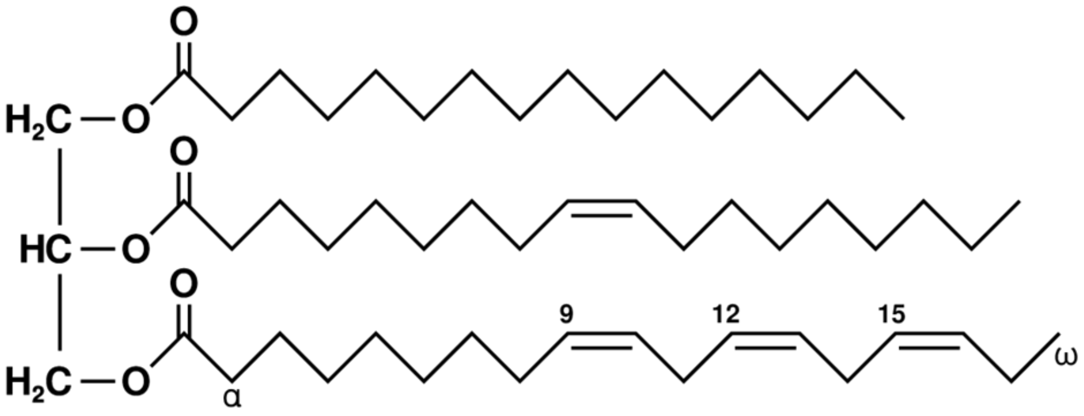


Figure 1 Structure of Triglycerides

The classification of Veg. oil according to the composition can be put as

- Saturated (palmitic acid, mysteric acid, stearic acid and lauric acid)
- Mono-saturated (erucic acid, oleic acid and petroselinic acid)
- Poly-unsaturate (lenolenic acid, lenoliec acid, ricinoliec acid, eleostearic acid and verolic acid).

Fatty acids are very important because of the fact that the properties of triglycerides and biodiesel fuels depends upon the quantity of fatty acids in molecules that is the soap formation in presence of NaOH or KOH [6].

Vegetable Oil Chemical Structure

```
H     O H H H H H H H H H H H H H H H H H
 \    | | | | | | | | | | | | | | | | | |
  C-O-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-H
 /|     | | | | | | | | | | | | | | | | |
H |     H H H H H H H H H H H H H H H H H
  |
  |
  |   O H H H H H H H H H H H H H H H H H
  |   | | | | | | | | | | | | | | | | | |
H-C-O-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-H
  |     | | | | | | | | | | | | | | | | |
  |     H H H H H H H H H H H H H H H H H
  |
  |
H |   O H H H H H H H H H H H H H H H H H
 \|   | | | | | | | | | | | | | | | | | |
  C-O-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-H
 /      | | | | | | | | | | | | | | | | |
H       H H H H H H H H H H H H H H H H H
```

Figure 2 Structure of Vegetable Oil

Table1 Physical Properties of Fatty Acids [3, 4, 5]

Fatty Acids	**Carbon No & Bond**	**Structure (Chemical)**	**Melting Point**
Lauric Acid	C_{12}	$CH_3(CH_2)10COOH$	43
Myristic Acid	C_{14}	$CH_3(CH_2)12COOH$	54
Palmatic	$C_{16:0}$	$CH_3(CH_2)14COOH$	62

Acid			
Stearic Acid	$C_{18:0}$	$CH_3(CH_2)16COOH$	69
Oleic Acid	$C_{18:1}$	$CH_3(CH_2)CH=CH(CH_2)7COOH$	13
Linoleic Acid	$C_{18:2}$	$CH_3(CH_2)_4CH=CH(CH2)CH(CH_2)7COOH$	-9
Linolenic Acid	$C_{18:3}$	$CH_3(CH_2)_2CH = CH(CH_2)CH = CH(CH_2)CH = CH(CH_2)7COOH$	-17
Eurcic Acid	$C_{22:1}$	$CH_3(CH_2)7CH=CH(CH_2)11COOH$	33

Table 2 Composition of Hydrocarbons in Different Vegetable Oils [7]

Veg. Oil	C12	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	C20:0 – C22:0	C22:0 – C22:1
Rapeseed	-	-	2-5	0.2	1-2	10-15	10-20	5-10	0.9	50-60
Soybean	-	0-3	7-11	0-1	3-6	22-34	50-60	2-10	5-10	-
Tallow	0.2	2-3	25-30	2-3	21-60	39-42	2	-	0.4-1	0.3
Peanut	-	0.5	6-11	1-2	3-6	39-66	17-38	-	5-10	-
Palm	-	1-6	32-47	-	1-6	40-52	2-11	-	-	-
Corn	-	0-2	8-10	1-2	1-4	30-50	34-56	-	-	0-2
Coconut	44-51	13-18	7-10	-	1-4	5-8	1-3	-	-	-

Selection of Feed

Our proposed vegetable oil was rapeseed oil as it is available easily all over Europe. The use of vegetable oil as fuel varies from country to country due to the fact of availability. Having more molecular weight, these vegetable oils have to be treated before use as diesel fuel. They have high kinetic viscosities which makes difficult to use them as it is because they are not fully injected and incomplete combustion takes place as a result of which it produces less energy and a lot of emissions. They also lack in the heating values as compared to diesel fuel obtained from fossil fuel.

The Reaction Processes

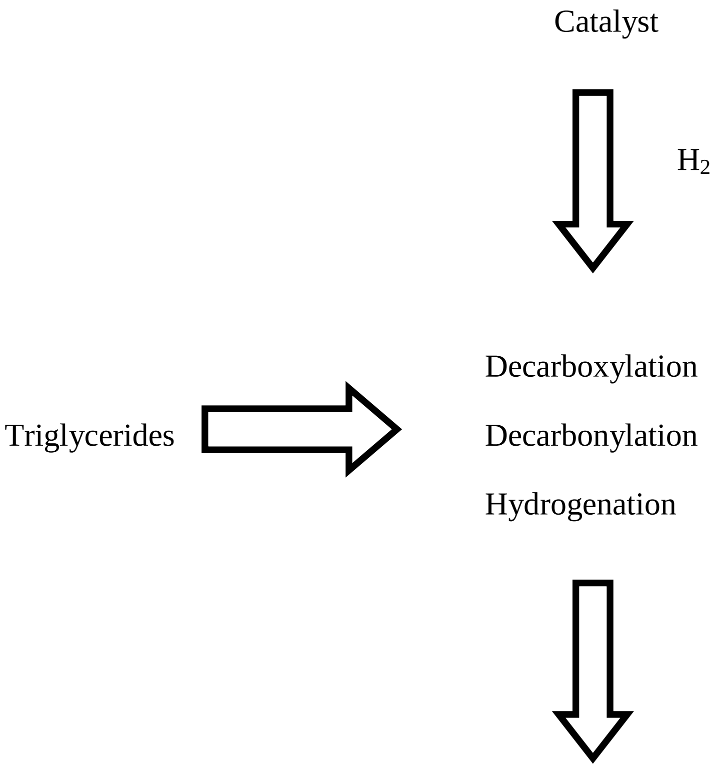
Hydrodeoxygenation

This process usually takes place at temperature range 300-600°C with high pressured H_2 in the presence of catalyst [8,9,10]. Mo based hydro-treating catalyst with Ni or Co as promoting agents, is widely used in the industry for this purpose.

In Hydro-deoxygenation, oxygen reacts with H_2 which gives out water and saturated C-C bonds and thus conversion of alkenes to straight chain alkanes from C_{12} to C_{18} is achieved in this manner. [11-15].They have high Cetane number (55-65) and gives better economy when blended with petro diesel [8].

Normally the process conditions are 40-150 bar pressure and 350-450°C. With this process the contaminants such as nitrogen, sulfur, oxygen and metals in liquid fuels are also removed.

Also the hydrogenation of aromatic compounds is avoided for it increases the use of H_2 and also reduces the Octane number for the fuel. Hydrodeoxygenation process increases the energy content and stabilizes the product. Main purpose is to reduce the formation of poly-unsaturates and products from trans-esterification where C=C is hydrogenated and alkanes are produced through different ways [16].



High Quality Diesel

Also isomerization of alkanes can take place during the process and most often the yield for C_{15} – C_{18} mono carbon straight chain alkanes is around 70% and the maximum theoretical yield for such products is up to 95% at optimal conditions.

$$R\text{-}CH_2\text{-}COOH = R\text{-}CH_3 + CO_2$$

$$R\text{-}CH_2\text{-}COOH + H_2 = R\text{-}CH_3 + CO + H_2O$$

$$R\text{-}CH_3\text{-}COOH + 3H_2 = R\text{-}CH_2\text{-}CH_3 + 2H_2O$$

In this step ester group reacts with hydrogen forming alkane and water. In hydro treatment, hydrogen reacts with oxygen containing groups and is exothermic reaction. Also de-oxygenation of fatty acid derivatives gives out CO_2, CO and aliphatic hydrocarbons with one carbon less than in fatty acid molecule.

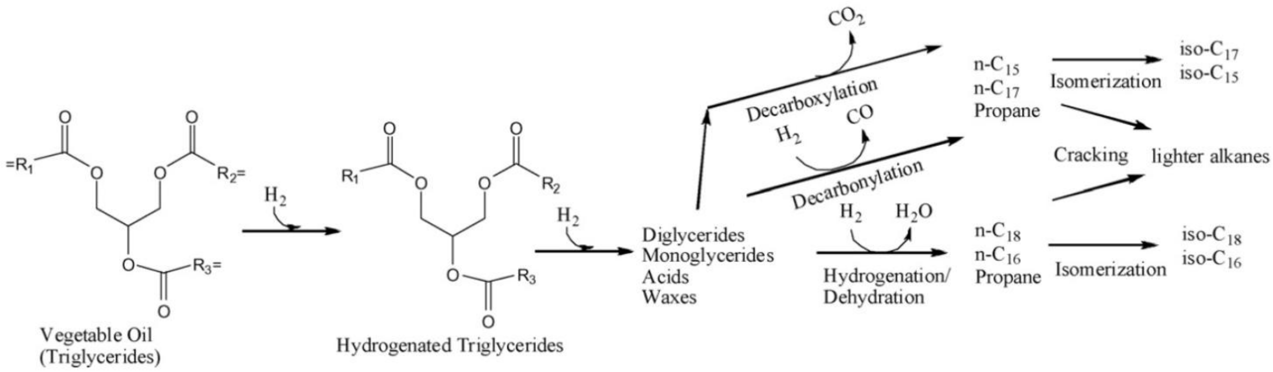


Figure 3 Estimated Reaction Network Catalytic Hydro-Processes of Rapeseed Oil [16]

Trans-Esterification

The reaction process in which triglycerides (major portion of vegetable oils) reacts with alcohols to make alkyl esters which is biodiesel and other products such as glycerol over the presence of catalysts.

This biodiesel can be used by blending it with petro-diesel without any engine modifications and can be blended up to 20% by volume [17, 18]. The intermediate compounds in this reaction are diglycerides and monoglycerides. Complete reaction is reversible and excess of alcohol is used normally 50-200% [19].

The presence of free fatty acids in the oil also leads to formation of soap and water by products when reacting with catalyst NaOH or KOH, which are highly unwanted and are very difficult to remove at the end of process.

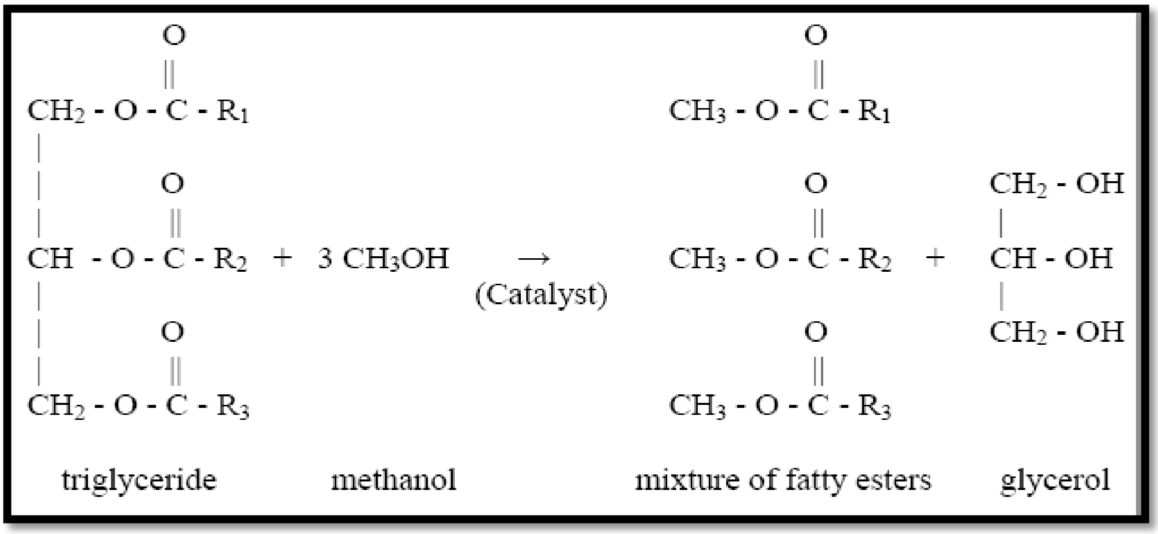


Figure 4 Reaction Mechanism for Trans-Esterification Process, [20]

Biodiesel

The process for biodiesel production comprises of reaction of natural oils with alcohol. They consist of mono alkyl esters of long chain fatty acids. The methyl esters from vegetable oils can be termed as biodiesel and can be produced from renewable sources such as animal fats, vegetable oils and waste cooking oils. Both chemically and physically, biodiesel can be compared to petro-diesel in terms of its properties also biodiesel is non hazardous, bio-degradable and more environmental friendly if used after proper refining process.

Table 3 Physical Characteristics of Biodiesel [20]

Calorific Value (KJ/Kg)	43760
Sulphur Content (mg/Kg)	154.8
Density @ 15°C (Kg/m^3)	822

Advantages & Disadvantages of Biodiesel

As far as disadvantages are concerned there is a temperature limit for biodiesel and in pure form it cannot be used at lower temperatures as it precipitates. Also it has low efficiency in terms of economy to power relation. It also emits more NOx during combustion which is harmful for environment.

While biodiesel has many advantages over petro-diesel like its flash point is higher 150°C which makes it safer for use and transport. There is reduced amount of VOCs which is because of the fact that it has no sulfur and aromatics. It has high Cetane number which is the measure of fuel quality with respect to ignition so there is better burning. It is clean source of energy with reduction of carcinogenic potential up to 95% and has highest BTU contents.

Biodiesel Properties

Table 4 ASTM Standards for Biodiesel [21]

Property	Limits
Pour Point °C	-15 to 10°C
Kinematic Viscosity @ 40°C	1.6 - 6.0 mm^2/S
Sulfur wt%	0.0 - 0.0024
Cetane Number	46 – 70
Lower Heating Value LHV (btu/lb)	15700 – 16735
Flash Point °C	150
Density g/cc	0.87 – 0.89
Higher Heating Value HHV (btu/lb)	16928 – 17996
Iodine No	60 – 135
Acid Value (mgKOH/g)	0.8

Production Processes for Biodiesel

There are two types of processes from which biodiesel can be produced. One is Batch processing and other is continuous processing [6].

Batch Process

During the batch process oil is fed to the reactor with alcohol and catalyst together and for certain time it is processed. In this time it is agitated with stirrer for proper mixing and reaction of catalyst. After a certain batch time, stirrer is stopped and solution is allowed to cool down which after settling gives out glycerol and esters and hence can be removed as two different layers. After the completion of the process, alcohol is recovered from the system to be used again and biodiesel is stored in some tank as required product. Also soft water is used to wash out the esters produced during the conversion of oil to biodiesel. Below is the schematic diagram for the biodiesel batch process.

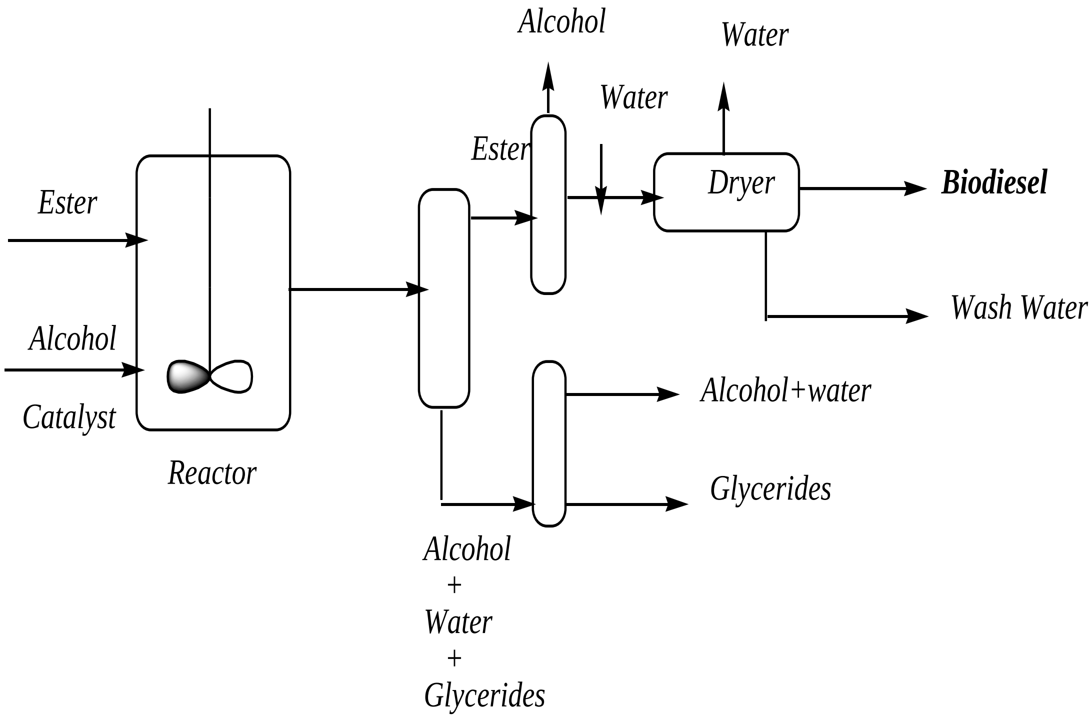


Figure 5 Batch Process Scheme

Continuous Process

For continuous process, continuous stirred tank reactors in series are being used which are equipped with efficient stirrers in order to attain the maximum yield and efficiency of the process. In this process, vegetable oil before use is due to the presence of free fatty acids which are removed by washing it with some strong acid. Also the catalyst sodium methaoxide is prepared for trans-esterification process. The schematic diagram for continuous process is given below.

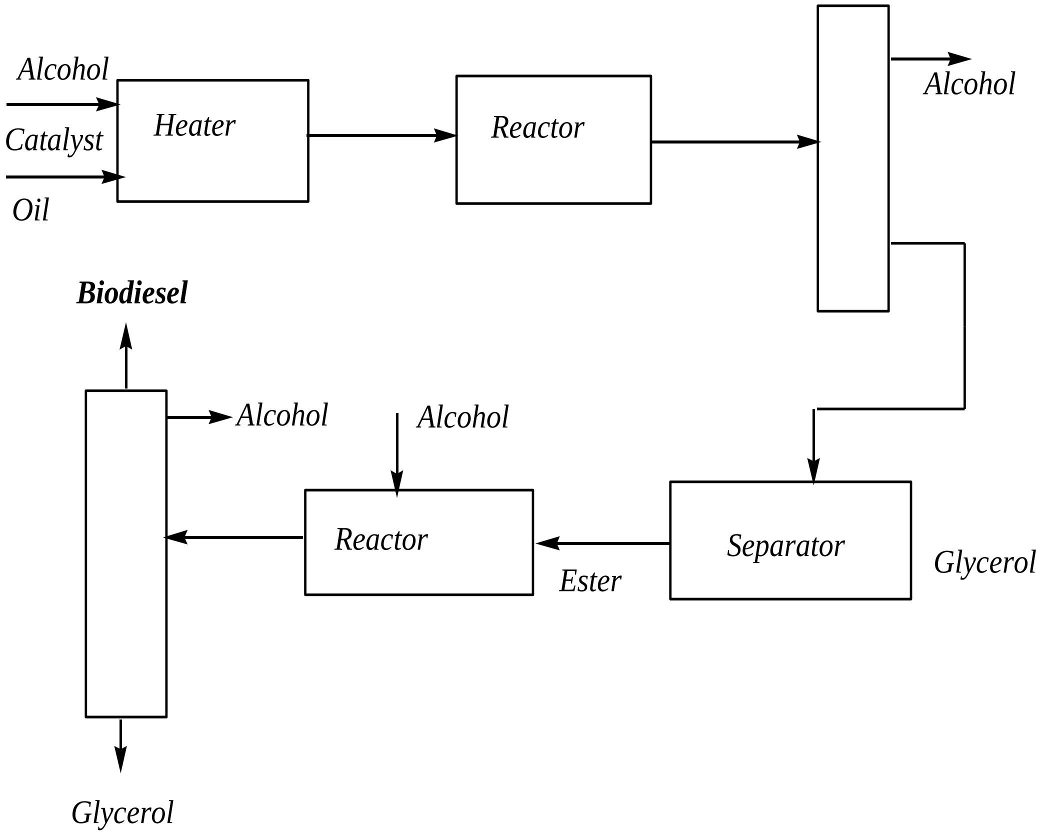


Figure 6 Continuous Process Scheme

Chapter 3 Experimental Setup & Analytical Equipment

The Reactor

Hydrogenation process was carried out in autoclave reactor with 300 ml volume which is equipped with a temperature controller and an electrical magnetic drive stirrer both from *Parr* instruments. If higher temperature limit is reached, the heating is stopped automatically and the temperature fluctuation can be ± 3 °C. The heating system consists of a heating mantle on the outside with a covering of aluminium shell with thermocouple connected to reactor (*Parr*). Below are the details of the autoclave reactor.

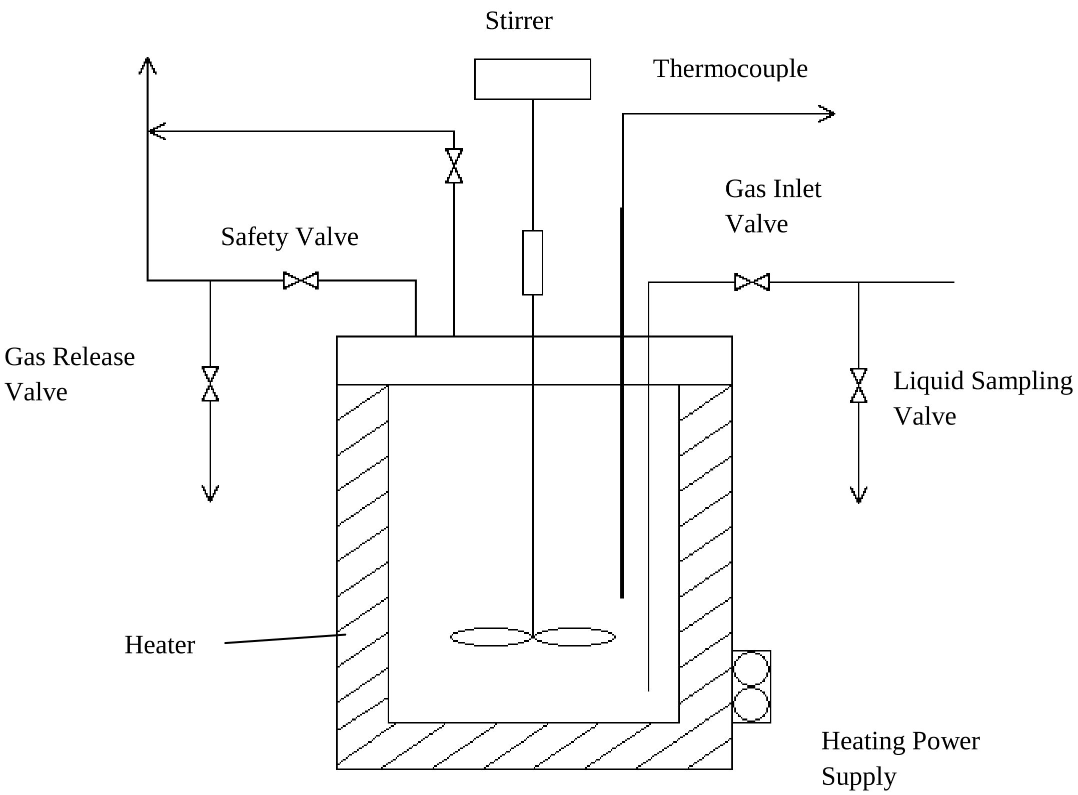


Figure 7 Autoclave Unit Scheme

Temperature Controller

The temperature control is also from Parr instruments, which is coupled with the reactor equipped with PID regulator from *Watlow systems*. Temperature itself has influence over the rate of reaction and activity of the catalyst. In order to study kinetics of the reaction, proper control over the reaction is must. To study the kinetics a good control over the temperature is a must.

Figure 8 Parr 4842, PID Temperature Controller

At the start of experiment, the desired temperature for the process is set from the controller keys and no stirring is applied until the set point is reached. This heating inside the vessel normally takes 35-60 minutes depending upon the set point. Also the stirrer is to be started little before the set point in order to avoid the rapid shooting of the temperature above desired set point and to stabilize the whole process. This is shown in the following figures.

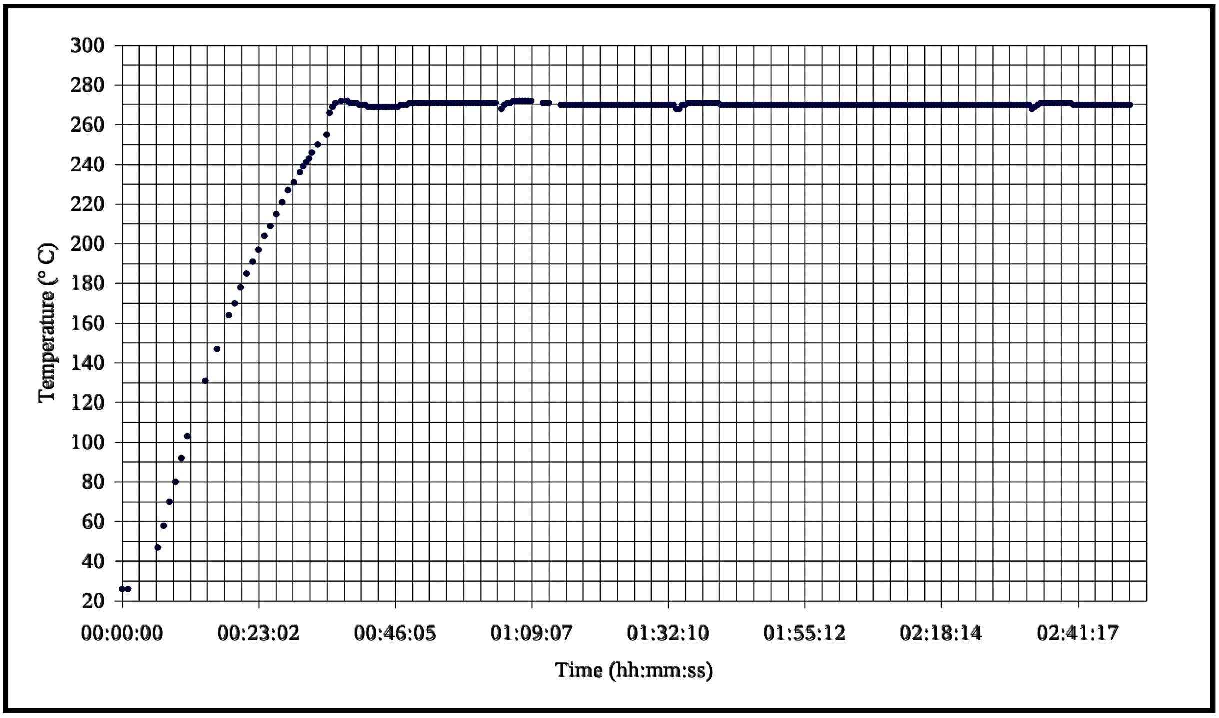


Figure 9 Temperature against Time; Set Point 270 ℃

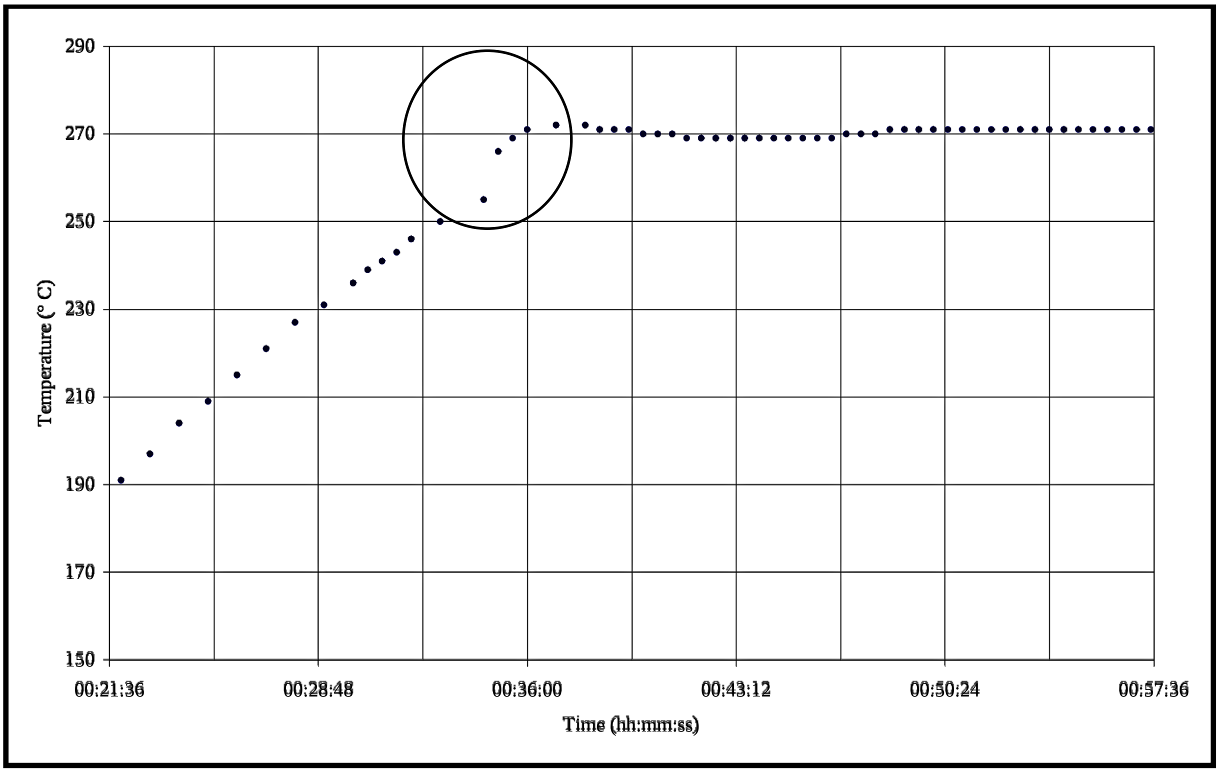


Figure 10 Disturbances caused by the stirrer to the thermal system; set point 270 ℃

Calcinations / Drying

Before the experiments all the catalysts have to be dried in order to avoid any moisture contents in the samples. Thus electric furnace is used for this purpose and usually the drying is achieved by putting the catalyst for overnight at temperature depending upon the condition and properties of catalysts.

Catalyst Activation

Apparatus Setup

The apparatus consists of fixed bed reactor with gas flowing upwards and at atmospheric pressure fitted with a vertical glass tube having diameter 25mm in electrical furnace housing to heat up this tube to a specified temperature. Gas from the bottom arises to the reactor through the pipe which is sealed with the help of silicon rubber to avoid any leakages and after passing the tube comes out from top. Packing of glass balls is used with 2 mm diameter supported by a stopper of glass wool to give uniform more surface are for better reaction with catalyst lying on this wool.

Catalyst Activation Process

During this process the catalyst (NiMo) is placed inside the tube which is packed with glass balls as packing material in order to contribute proper flow of H_2S gas across the tube. 1 gram of dried catalyst is placed on the upper side of glass wool layer in the tube and H_2S with 10% by vol. mixture in H_2 gas is used for sulfidization process which passes through the tube for around 200 minutes with temperature of 400°C.

Figure 11 Catalyst Activation Apparatus

After this catalyst is left for overnight with nitrogen gas flowing through the system so that process takes ample time to achieve desired catalyst condition and to cool it down to ambient temperature. The flow for H_2S gas is min 240 ml/hr and the complete operation takes about 24 hours replacing H_2S with N_2 after 3 hours. To achieve the process temperature, tube is fixed with a thermocouple and PID controller. This activation of catalyst is necessary for increasing the reactivity limited time of batch process.

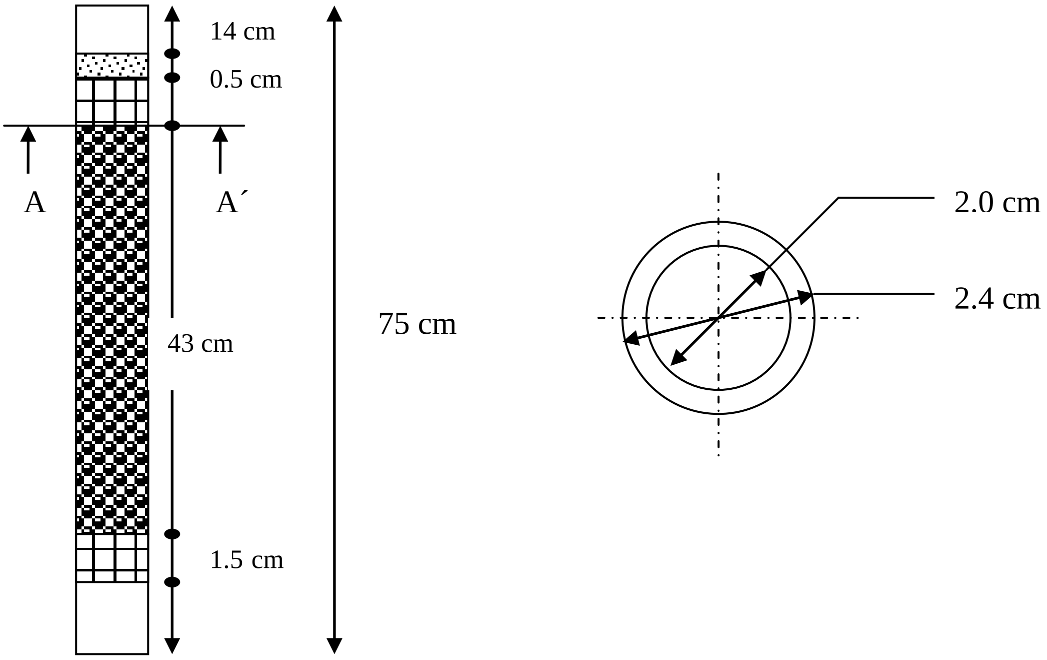


Figure 12 Sulfurization Tube Specifications

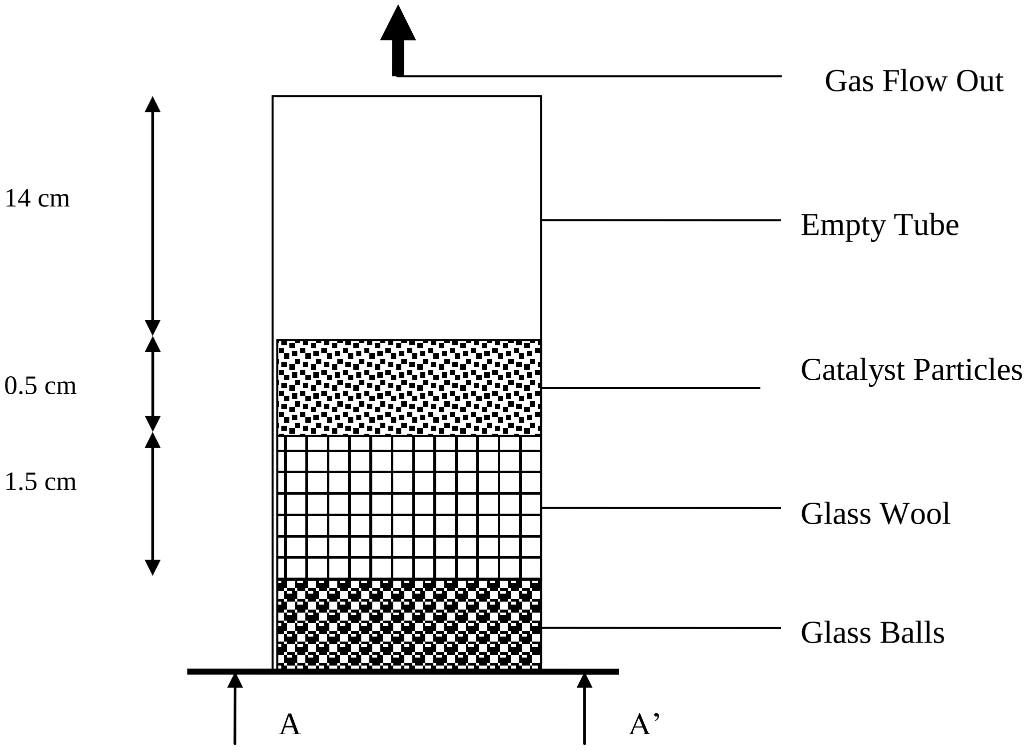


Figure 13 Sulfudization Reactor Part

Catalyst & Pore Specifications

Three different catalysts have been considered for the comparison in order to study the effect on yield and products at the elevated temperature and constant pressure. Pressure drop and channel formations are very much dependent on the shape of catalyst with small spherical shape causing large pressure drops over fixed bed reactors and ring shape can form channels in the bed.

NiMo-S/Al_2O_3 Catalyst

The catalyst used was Trilobe HDN-60 (NiMo/γ-Al_2O_3) from Cirterion Catalysts. NiMo-S/Al_2O_3. Composition for the catalyst material is 2-3 % Ni, 12-14 % Mo and rest % age is for γ-Al_2O_3 support which is 83-86 %. Where Mo acts as active element and Ni plays the role of promoting agent in the catalyst. BET surface area 157.5873 m^2/g, single point adsorption total volume of pores 0.343004 cm^3/g with pore diameter of 2492.019Å or 0.00002492019 cm.

Beta-Zeolite Catalyst

Beta – Zeolite is 2 wt% Pt on Zoelite which is 40 wt% with γ-Al_2O_3 extrude (disprol & locron) 60 wt%. BET surface area 248.3468 m^2/g and single point adsorption total volume of pores 0.224422 cm^3/g with pore diameter of 1646.250Å or 0.0000164625 cm.

Palladium Carbon Catalyst

The specifications for this are Palladium 5 wt% on activated carbon, 205680 from Sigma – Aldrich (Pd/C). BET surface area 935.7183 m^2/g and single point adsorption total volume of pores 0.742960 cm^3/g with pore diameter of 899.906Å or 0.00000899906 cm.

Gas Chromatography/ Product Analysis

Liquid Analysis

In this technique flame ionization detector is used to observe the separated components in the given sample and this is done on the basis of retention time method RT which can be calibrated to see the amount of components with hydrogen as a career gas. FID is most widely used GC technique for the analyses of different mixtures both in liquid and gas forms.

Figure 14 GC Varian 3400

The retention time of a component is influenced by temperature on the basis of ionization of the components. With the increase in temperature of the column, components are displayed at different RT's. The conditions at which the equipment is operated are listed below in table. 0.5 µl of sample is injected each time for the analyses. For liquid analysis of samples, GC was used to obtain the weight % of the components with respect to the retention time for classification of compounds present in the product samples at different time. GC Varian 3400 was used in this case which was equipped with flame ionization detector (FID) and this was integrated with Varian 4270 printer for graphic representation of the analysis. Samples were injected with micro syringe.

Table 5 Gas Chromatography Conditions

Injector Temperature	325 ºC
Detector Temperature	325 ºC
Initial Temperature	40 ºC
Initial Stabilize Time	2 min
Rate	18 ºC/min
Hydrogen pressure	6.2 bar
Nitrogen pressure	6.2 bars
Internal Standard	n-Hexadecane
Injection	On Column
Final Holding Time	10 min

Gas Analysis

Similarly gas samples taken at the end of each experiment were also studied using live online Clarus 500 which is connected to 600 link switch controllers for integration of graphical representation. GC comprises of FID for hydrocarbons & thermal conductivity detector (TCD) for detecting the amount of components in the gas phase like CO, CO_2, H_2, N_2, CH_4.

Table 6 Clarus 500 Conditions TCD

Initial Temperature	40 ºC
Oven Temperature	60 ºC
Rate	8 ºC/min
Carrier Gas	Helium (6.2 bar)
Nitrogen pressure	6.2 bar
Initial Holding Time	8 min @ 40 ºC

Injection	On Column
Final Holding Time	2 min @ 60 ºC
Sample Amount	5 µl

Table 7 Clarus 500 Conditions FID

Initial Temperature	40 ºC
Oven Temperature	60 ºC
Carrier Gas	H_2 (6.2 bar)
Nitrogen pressure	6.2 bar
Holding Time	15 min @ 60 ºC
Sample Amount	5 µl

FTIR - Analysis Fourier Transform Infrared Spectroscopy

This technique is used widely for studying the infrared spectrum for liquids, gas or solids. During FTIR analyses mainly four different groups were studied due to the presence in the samples. These are as under

- Alcohols
- Ethers & Esters
- Carboxylic Acids and Aldehydes

The wavelengths for these groups which have been obtained from literature are given here in this table to identify the components [22**].**

Table 8 Infrared Absorption Frequencies

Functional Groups	**Wave Number cm^{-1}**
Aldehydes	2830 - 2695 cm^{-1} (C-H stretch) 1740 – 1720 cm^{-1} (C=O stretch)
Ethers & Esters	1300 – 100 cm^{-1}(C-O stretch)
Alcohols	3500 – 3200 cm^{-1}
Carboxylic Acids	3300 – 2500 cm $^{-1}$
Trans	980 – 960 cm $^{-1}$
CIS	730 – 675 cm $^{-1}$

Chapter 4 Experimental Procedures

Methodology

In all the experiments, first step for the process was to prepare the catalyst which was followed by sample preparation for batch reactor and finally the results were analysed through GC & FTIR for the various samples which were taken at the time of experiments. Each experiment was subject to 8 samples at different time intervals to see the extent of reaction. Total of 10 experiments were carried out with three different catalysts already described above in previous chapter. The temperature range was 280-360°C and the hydrogen pressure was constant @ 40 Bar for all the experiments.

Sample Preparation

The feed used for all the experiments was the mixture of 20 wt% vegetable (rapeseed) oil with 80 wt% decane as solvent. And each time 150 ml of the sample was taken to place in vessel for the batch reactor. Decane was added in order to decrease the viscosity of the mixture for it is to be easier to analyse in GC. Also decane had no reaction with oil or catalyst. Decane used in the preparation of sample as solvent was from Sigma Aldrich and was 99.9% pure.

Catalyst Sulfidization

For each experiment, catalyst was prepared each time. For preparation, catalyst was first dried in furnace for overnight so that there is no moisture/water content. After this it was placed for activation process for 3 – 4 hours and allowed to cool for 20 hours in the presence of nitrogen gas. But this was only done with NiMo-S/Al_2O_3 catalyst and rest of the catalyst like Pd/C & Beta Zeolite doesn’t require to be activated still they have to be dried to take out the moisture contents. After this sulfidization 1 gram of catalyst was placed in the vessel with 150ml sample.

The Experiments

All the experimental work has been carried out in autoclave batch reactor with 300ml capacity for Parr Instruments Company, USA. The equipment was first thoroughly cleaned and washed for the test run in order to see any leakages or temperature offshoots when the stirrer is switched on. So the stirrer is switched on about 10°C before the set point in order to avoid any instant disturbances during the process. Each experiment was done with constant pressure of 40 bar and at different temperatures starting from 280°C to 360°C.

Air Tightness

The vessel was filled with 150ml of feed mixture and 1gram of catalyst is added in cases of all the three catalysts. Then the seal (flexible graphite gasket *Parr*) was placed between the joints of reactor for avoiding the leakage or any pressure loss during the process. This graphite gas kit has to be replaced for each run of experiment. So after setting the desired pressure with H_2 by releasing the previous gas from the reactor so that there is no air in the system, the reactor was air tight with clamps and was set to go. After this the desired temperature was set for each run separately like first for 280°C and left for 45-50 minutes to reach to the set point. During this the increase in pressure was also observed due to heating of vessel.

Figure 15 Autoclave Batch Reactor

Now just before the set point of temperature is reached the zero sample is taken which is at 0 mins and stirrer is turned on which has constant rotation speed. Samples were taken at different periods of time like 15, 30, 60, 90, 120,150 and 180 minutes which makes it 3hour operation.

Liquid Sampling

For taking the liquid samples from the reactor, stirrer is first switched off every time to avoid any splashing of liquid and the catalyst loss. The valve for liquid samples is opened slowly and cautiously due to high pressure inside the vessel. Also first droplets are not taken as sample because of the fact that they may contain impurities from previous products inside the sample valve. All the samples were taken into small bottles with great care so that there is no catalyst in the sample taken this was done by slowly opening the sample outlet. The sample size was approx. (1 – 2) ml in each case after discharging first droplets. The sample time and pressure was noted after each sample as observed that pressure inside of reactor decreases every time the valve is opened. In order to avoid any release of catalyst while taking samples, the stirrer was shut down for a few seconds. This also helps to prevent the clogging of catalyst particles into the sampling valve.

Table 9 Experimental Run Plan

Experiments	Temperature Conditions	Catalyst Type
5	280°C, 300°C, 320°C, 340°C, 360°C	NiMo/γ-Al_2O_3-S
4	300°C, 320°C, 340°C, 360°C	Pd/C
1	360°C	Beta - Zeolite

After all the samples are taken, they are analysed with the help of GC also the product gas from the chamber is taken to study the components of the product gas.

Chapter 5 Results & Discussion

Graphical Representations

Gas Chromatography Liquid Samples – Beta Zeolite

The graphic representation clearly shows that only stearaldehyde formation took place while at 360°C and 40 bar so this means that conversion to hydrocarbons was very low and was only as a result of thermal reactivity. This can be due to the fact that pore diameter in this case is so small that the catalytic activity is very limited.

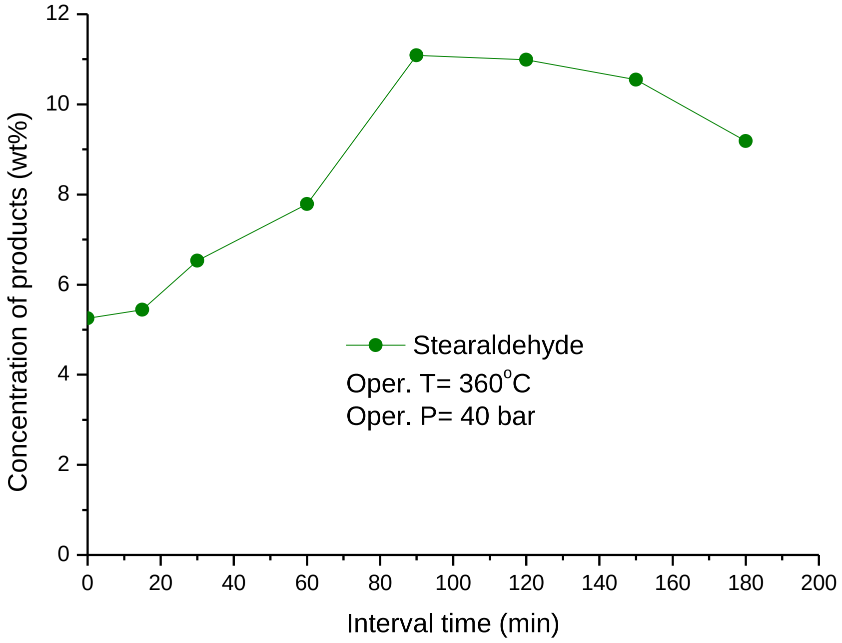


Figure 16 Pt/β - Zeolite 40 bar, 360 °C

Gas Chromatography Liquid Samples - NiMo-S/Al2O3

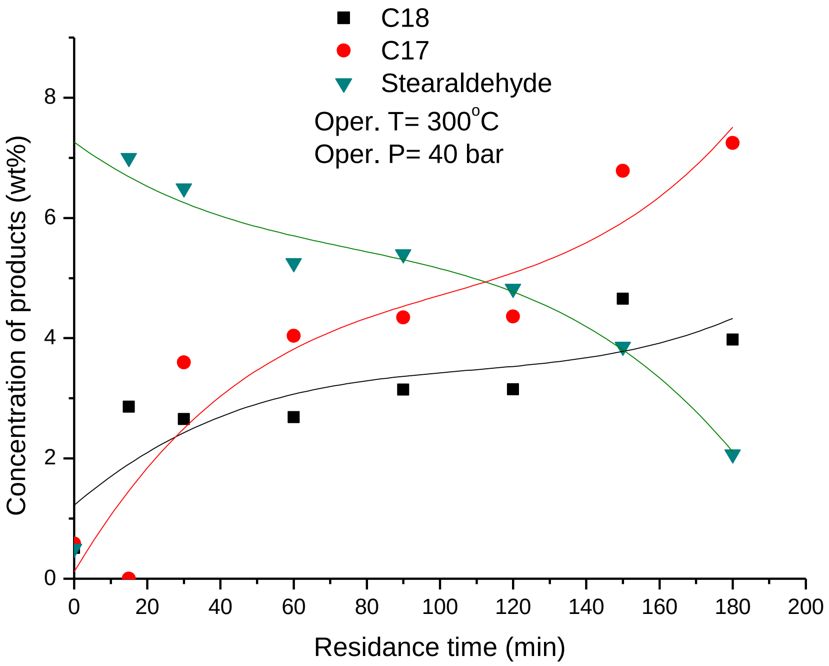


Figure 17 NiMo-S/γ-Al$_2$O$_3$ 40bar, 300 °C

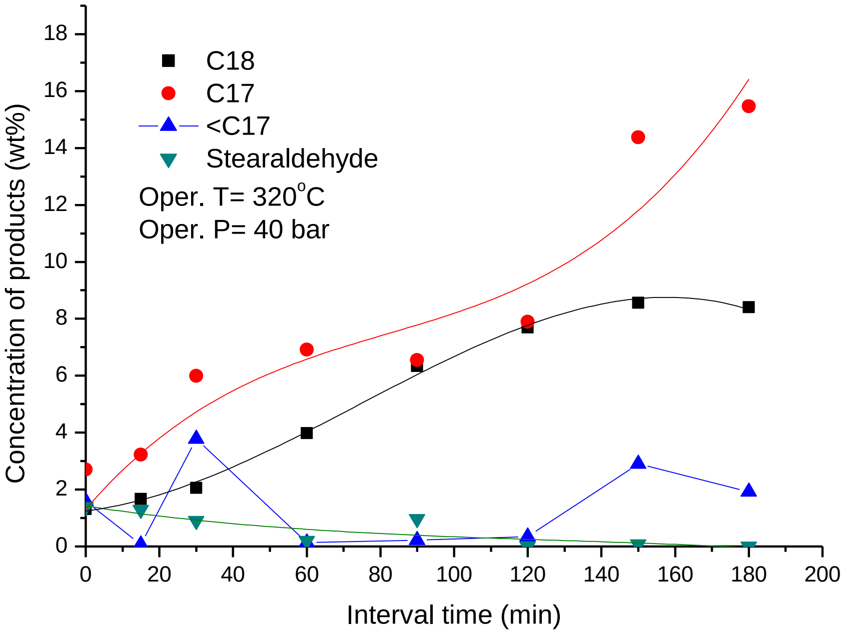


Figure 18 NiMo-S/γ-Al$_2$O$_3$ 40bar, 320 °C

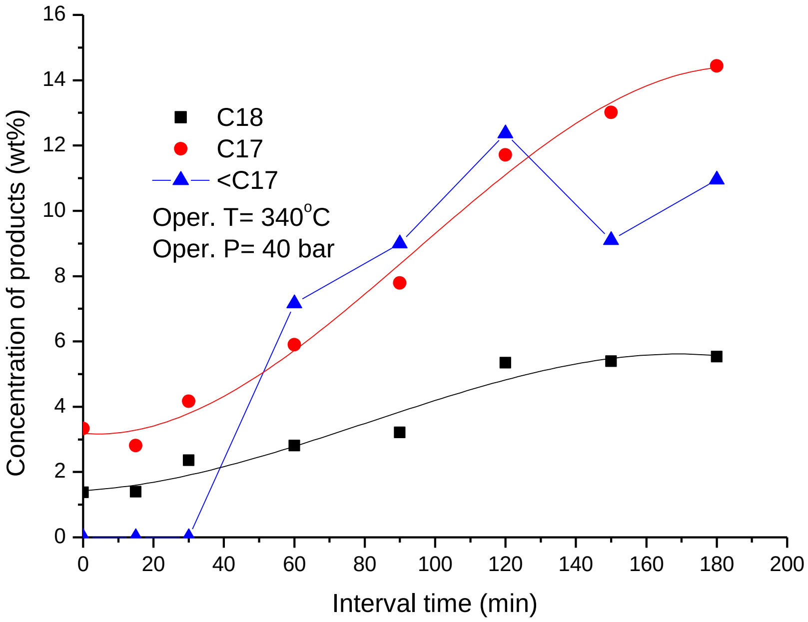


Figure 19 NiMo-S/γ-Al_2O_3 40bar, 340 °C

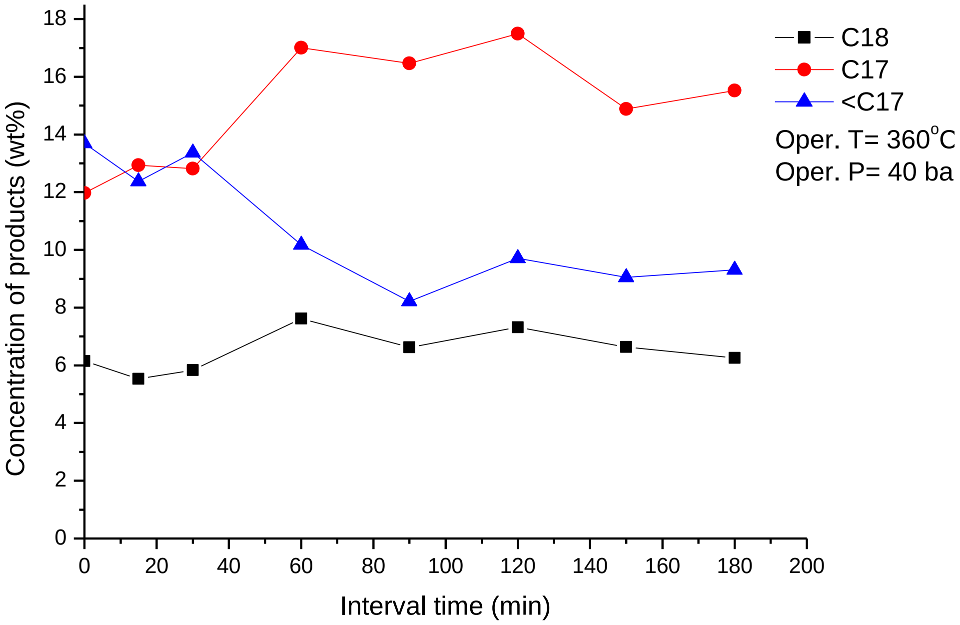


Figure 20 NiMo-S/γ-Al_2O_3 40bar, 360 °C

The conversion of vegetable oil into required hydrocarbons in the case of NiMo-S/γ-Al_2O_3 catalyst was most appropriate for the given temperature and pressure. It was observed that the yield of C_{17} and C_{18} kept on increasing up to 360°C and was max at this temperature with 40 bar pressure. Also the production of stearaldehyde was absent at 340°C and 360°C. It was only formed at lower temperatures and decreased with increase of temperature. So complete conversion is taking place at elevated temperatures which describes both thermal and catalytic activity.

Gas Chromatography Liquid Samples – Pd/C

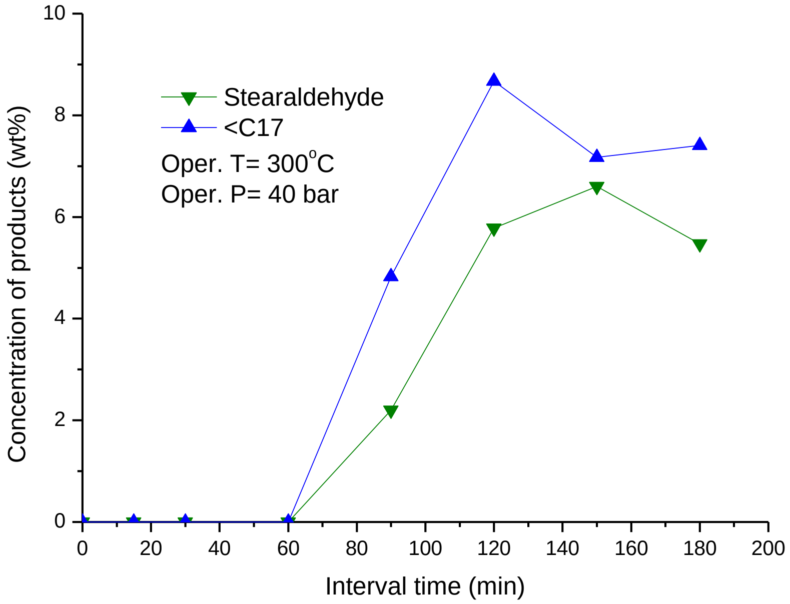


Figure 21 Pd/C 40 bar, 300 °C

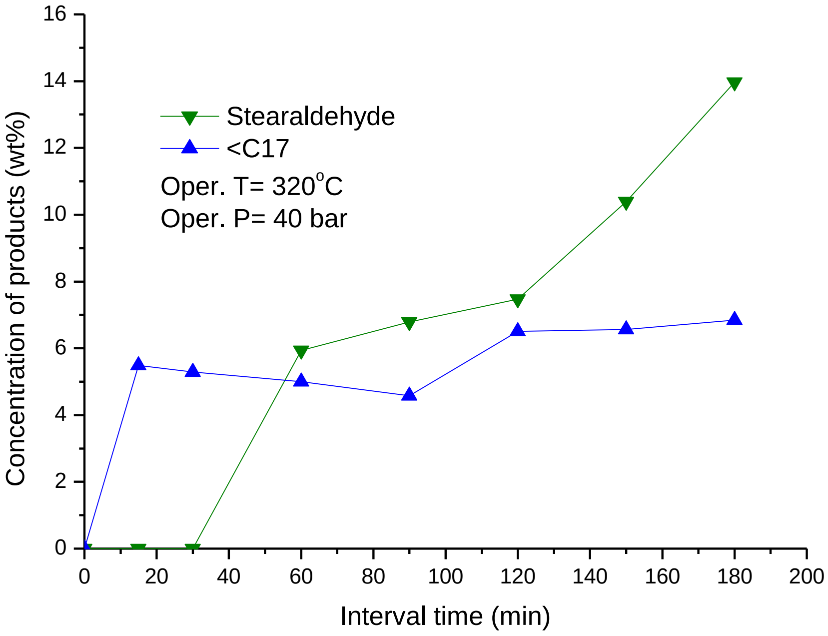


Figure 22 Pd/C 40 bar, 320 °C

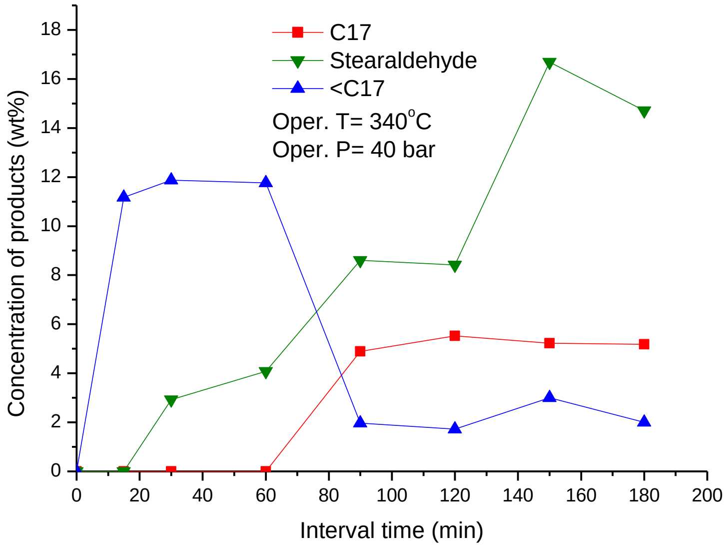


Figure 23 Pd/C 40 bar, 340 °C

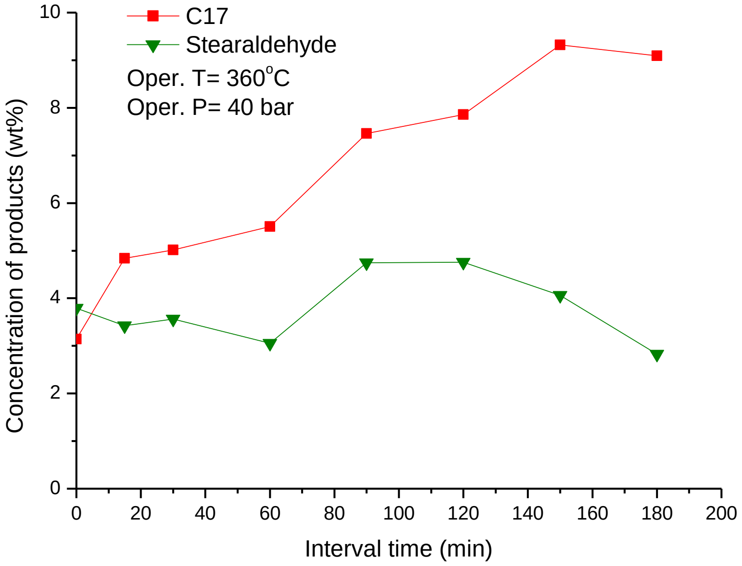


Figure 24 Pd/C 40 bar, 360 °C

In case of Pd/C, formation of intermediate compound which is stearaldehyde was found to be high due to the limited reactivity of the catalyst and catalyst characteristics. Also C_{17} was absent until the temperature of 340°C was reached and even at high temperatures, the yield for C_{17} was quite low so one can say it's because of mostly thermal activity.

Gas Chromatography Gas Samples - NiMo/γ-Al2O3

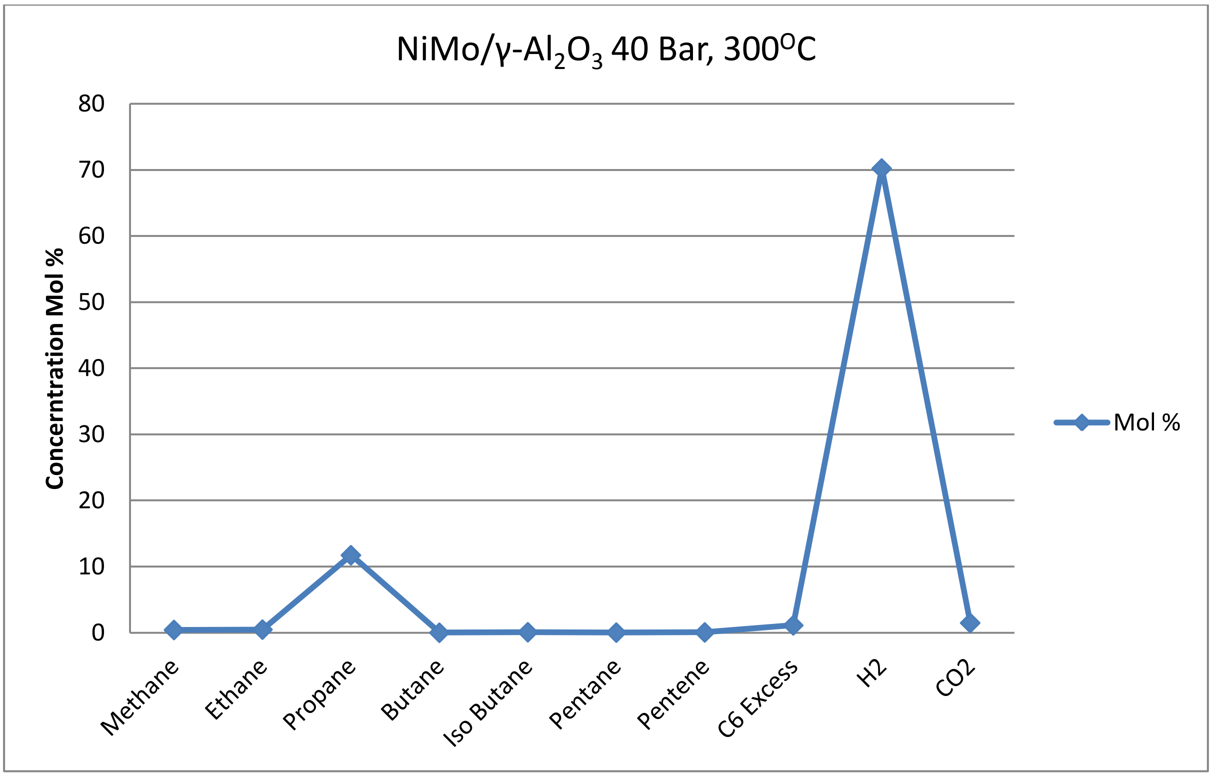


Figure 25 NiMo-S/γ-Al$_2$O$_3$ 40bar, 300 °C

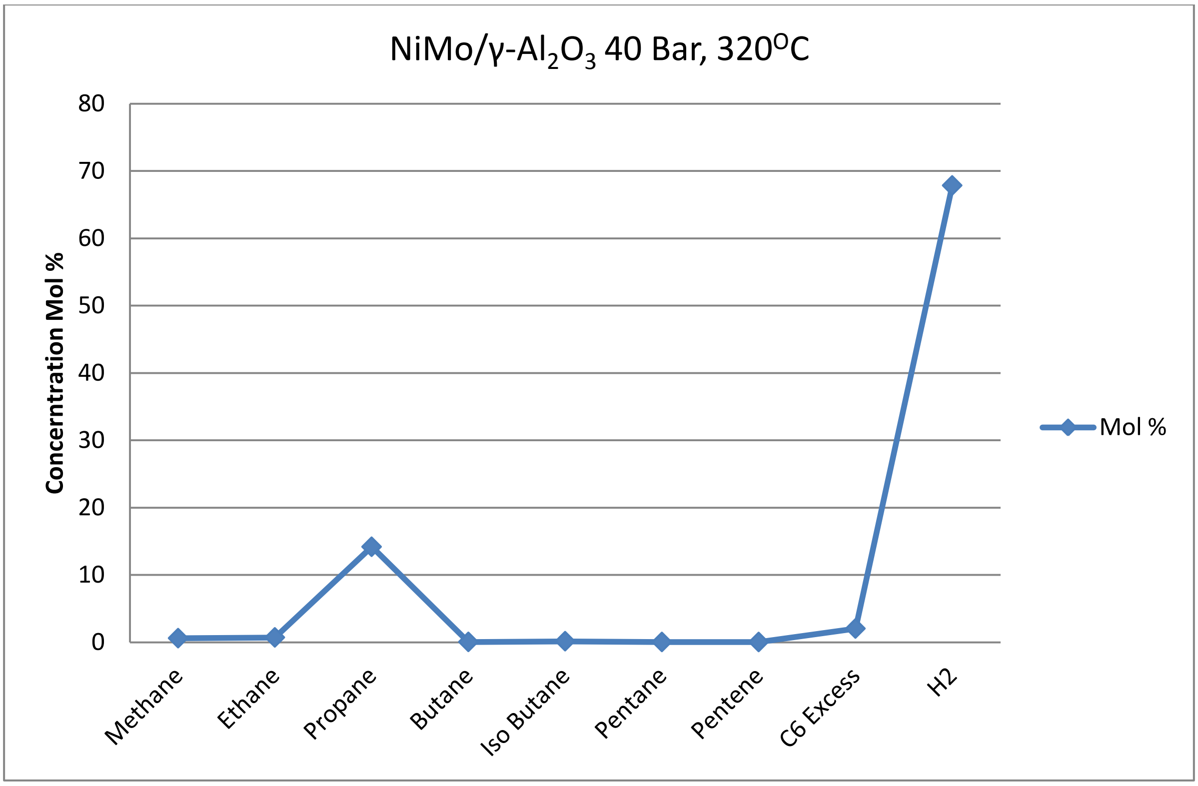


Figure 26 NiMo-S/γ-Al$_2$O$_3$ 40bar, 320 °C

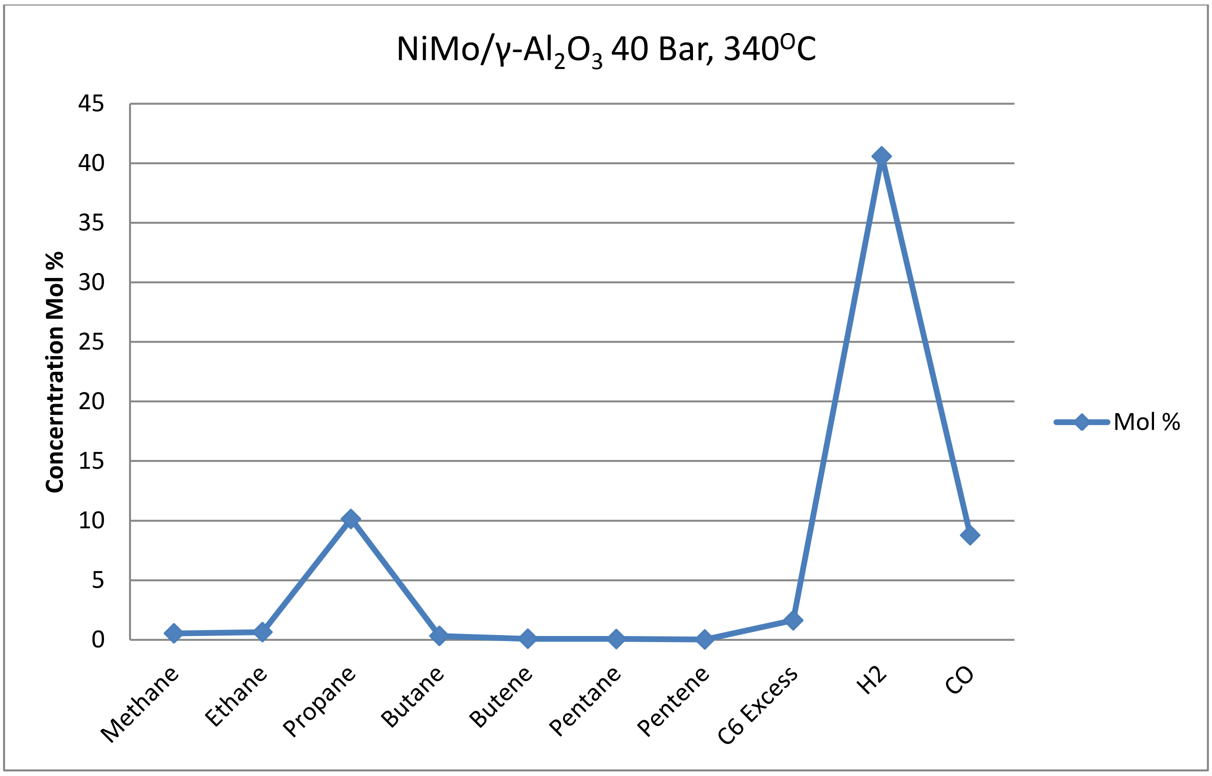


Figure 27 NiMo-S/γ-Al$_2$O$_3$ 40bar, 340 °C

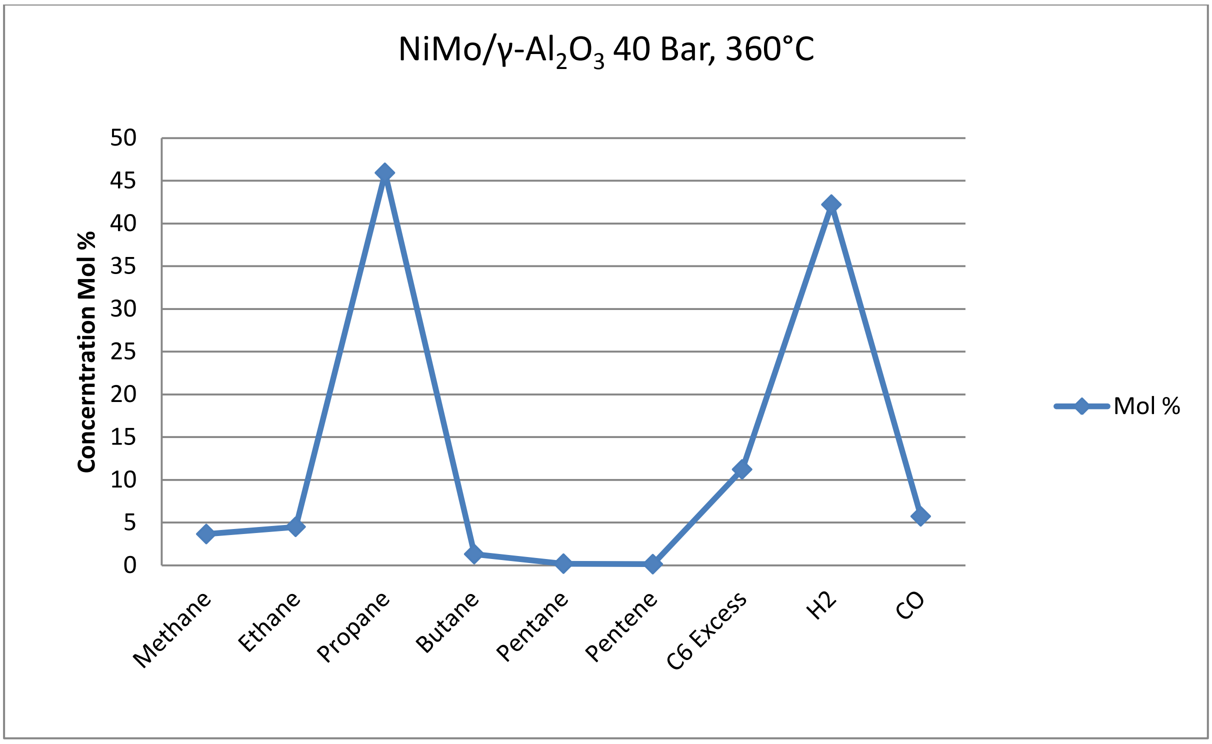


Figure 28 NiMo-S/γ-Al$_2$O$_3$ 40bar, 360 °C

High propane formation at 360°C due to sudden catalytic activity in the reaction chamber was observed.

Gas Chromatography Gas Samples – Pd/C

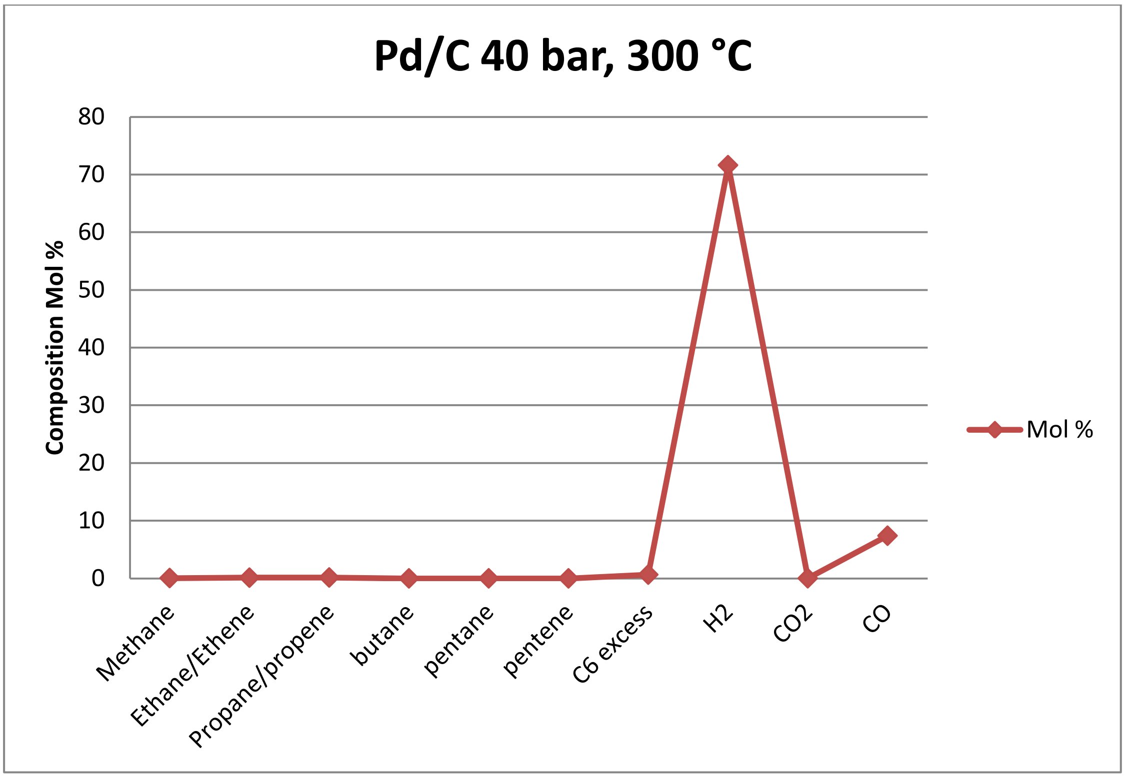


Figure 29 Pd/C 40bar, 300 °C

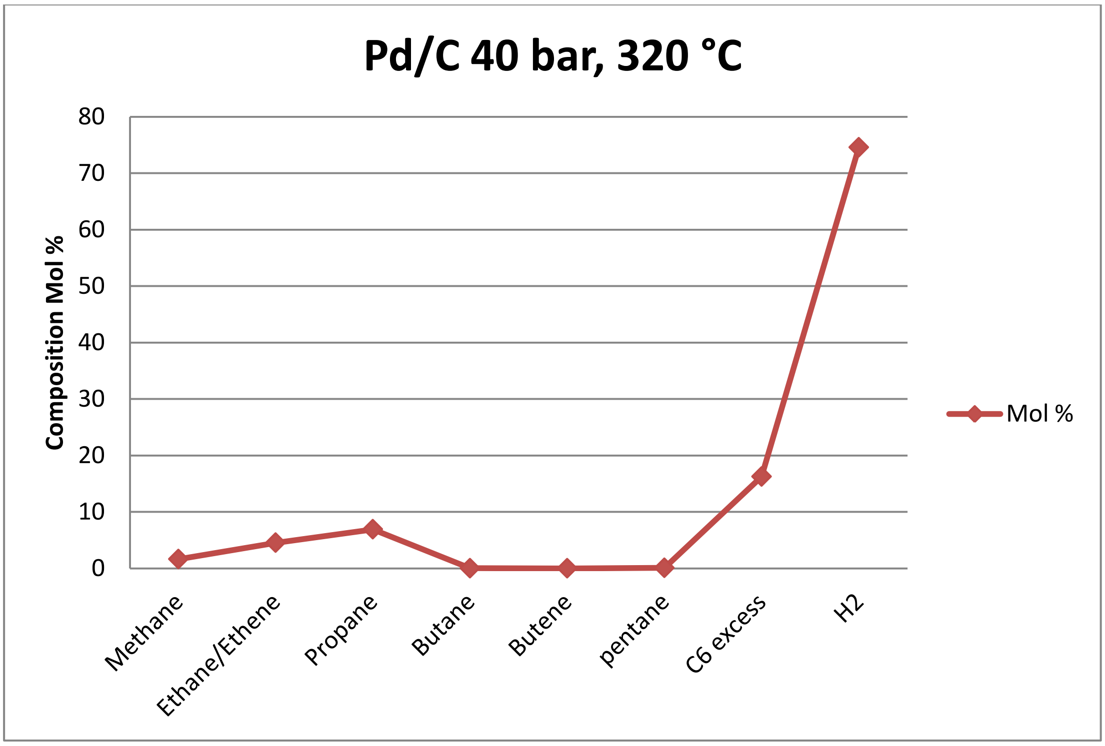


Figure 30 Pd/C 40bar, 320 °C

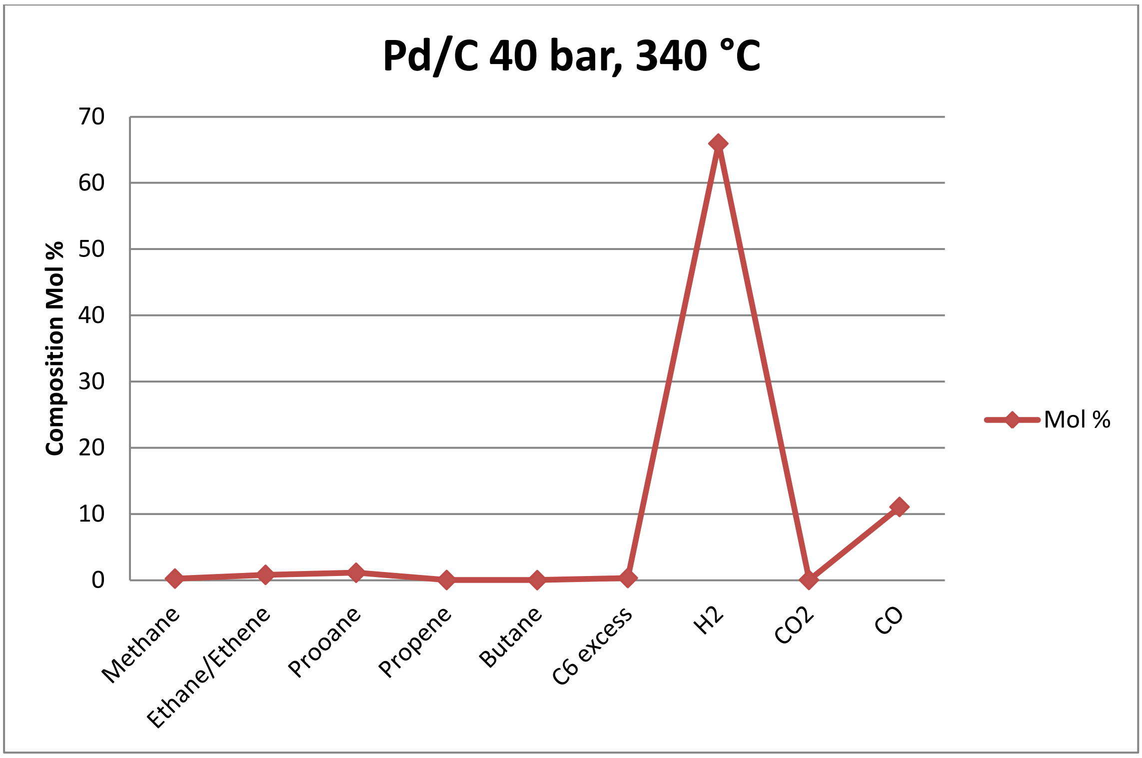


Figure 31 Pd/C 40bar, 340 °C

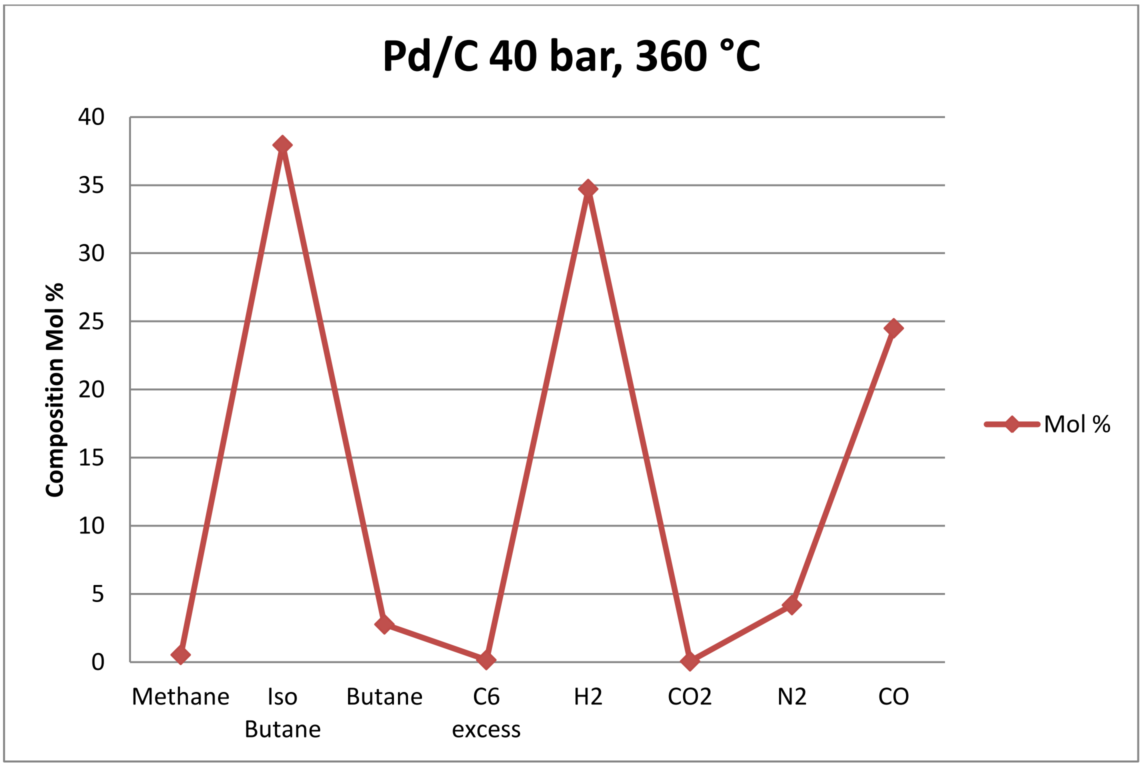


Figure 32 Pd/C 40bar, 360 °C

In the case of gas products of Pd/C catalyst, formation of propane was observed and even iso-butane at high temperature that also shows some catalytic activity.

Gas Chromatography Gas Samples – Beta Zeolite

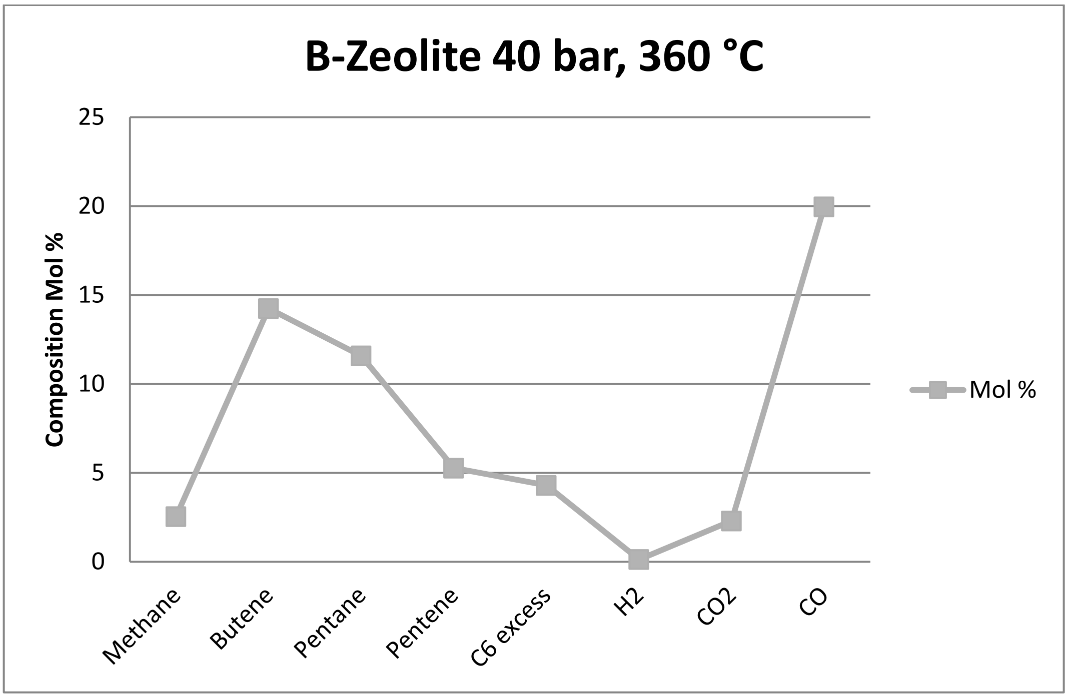


Figure 33 Pt/β - Zeolite 40bar, 360 °C

Gas product for Pt/β-Zeolite, we have higher hydrocarbons like butane and pentane rather than ethane which mean that there is a lot of thermal activity going on at the interface of the two phase liquid and gas. This can be due to the cracking of Decane in the sample. Also the amount of CO is quite high in the product as compared to other two catalysts with limited H_2 reaction.

FTIR Analysis Results

In the following figures, the peaks show the presence of different components in the liquid product. Mostly there were different types of alkanes found with prominent presence of aldehydes in Pd/C and Pt/β-Zeolite cases. Presence of Nitro compound in Pd/C case is due to the pyridine mixed to reduce the melting point of sample.

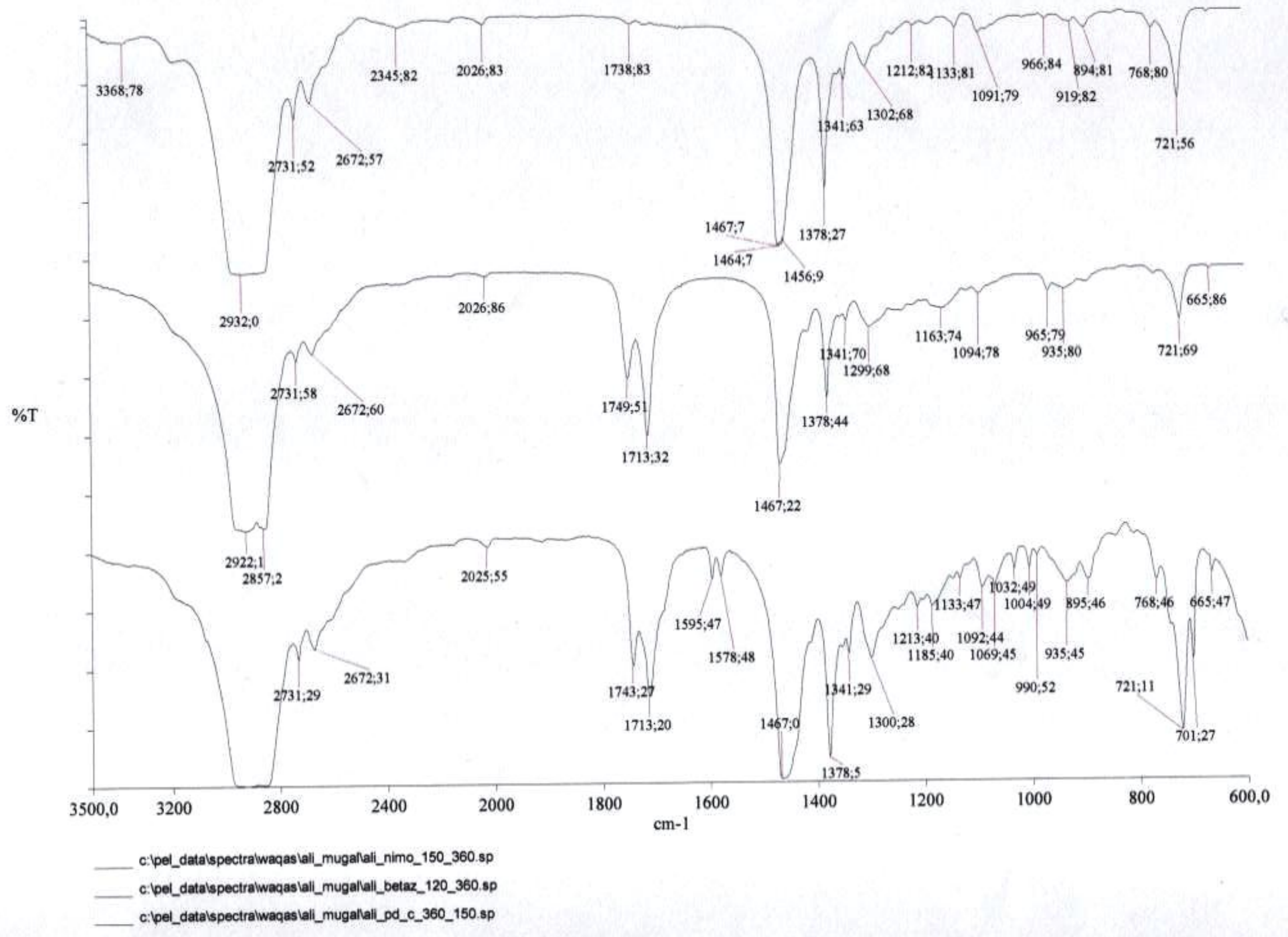


Figure 33 FTIR NiMo-S/γ-Al_2O_3, Pt/β – Zeolite & Pd/C

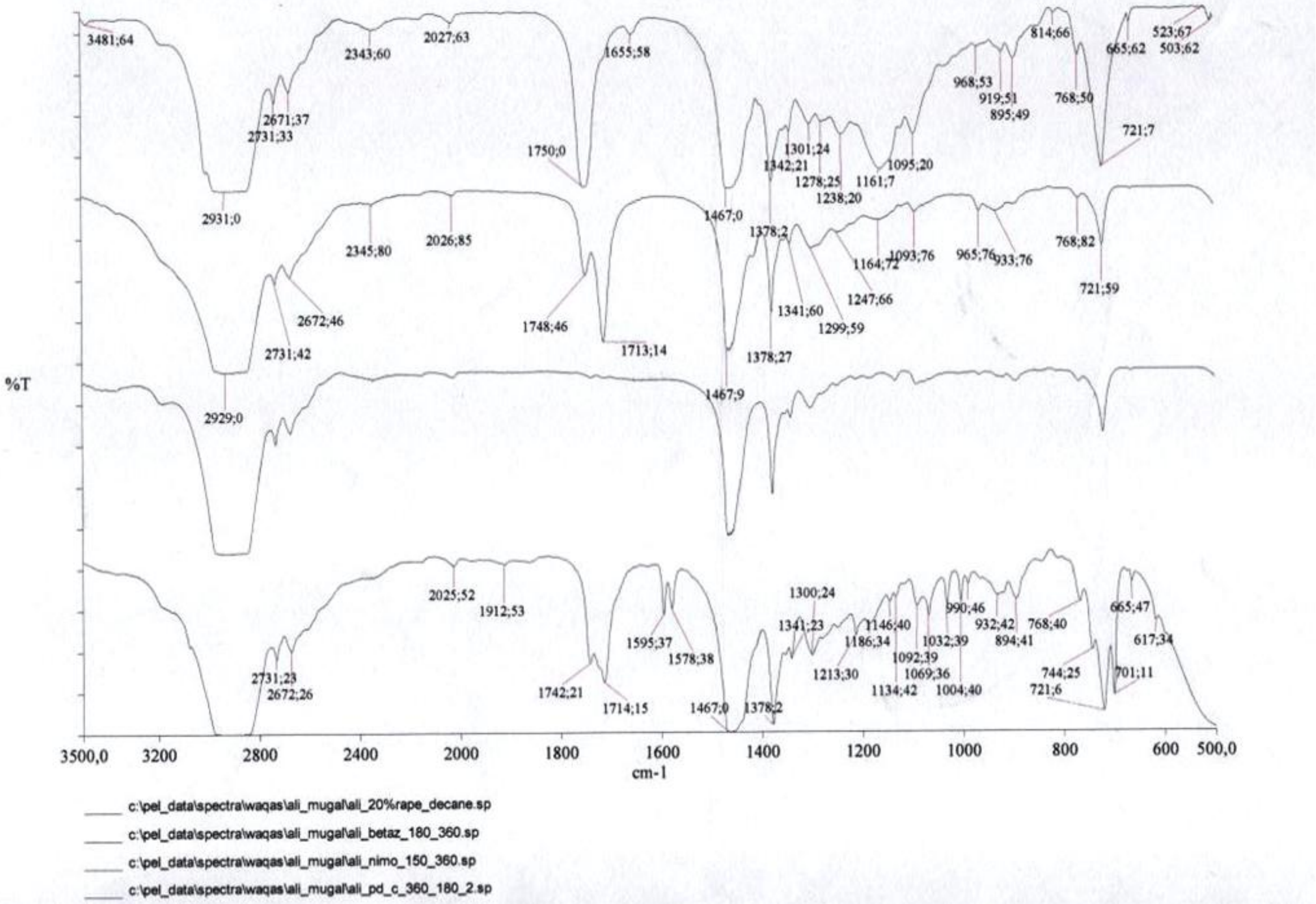


Figure 34 FTIR Rapeseed Oil (20%), NiMo-S/γ-Al_2O_3, Pt/β – Zeolite & Pd/C

Different stretches for corresponding peaks / components are

- C-H stretch Alkanes 2929
- H-C=O: C-H stretch Aldehydes 2731
- C-H bend Alkanes 1467,1378
- C-H rock Alkanes 721
- C=O stretch esters, Saturated Aliphatic but not in case of NiMo 1740-1750
- C-C stretch ring Aromatics in Pd/C small amount 1595
- N-O stretch Nitro compounds in Pd/C small amount 1578

Conclusions/Future Recommendations

Comments

The product distribution was varied on both catalysts. The selectivity of C_{17}, which was more dominating due to thermal decomposition, plays crucial role in the reaction mechanism. Partial hydrogenation was observed with Pd/C catalyst, but better selectivity obtained with NiMoS/γ-Al_2O_3.

The catalytic reactivity was low as compared to thermal reaction which allows the formation of Stearaldehyde as the intermediate compound which in case of Pd/C was quite prominent due to thermal activity. In case of NiMo-S/Al_2O_3, the catalytic reactivity was higher than other two catalysts because of larger pore diameter and pore diffusion.

Pd/C catalyst could be of interest economically but it gives low yield and products have very high melting point. However, if activated, may give good results but due to large molecules in structure of vegetable oil, the reaction will still be limited.

With Beta Zeolite catalyst the results were not so good in terms of yield for C_{18} as there was very little conversion but it could be of interest with high temperature like above 360°C and at high pressure than 40 bar. Also beta Zeolite was used with Pt which has very low reactivity, other element with higher reactivity should be used like rhodium but then it will be more expensive.

More advanced and better analytical setup is required for analysis of products due to chance of high error in GC results especially when it comes to the liquid sample analysis.

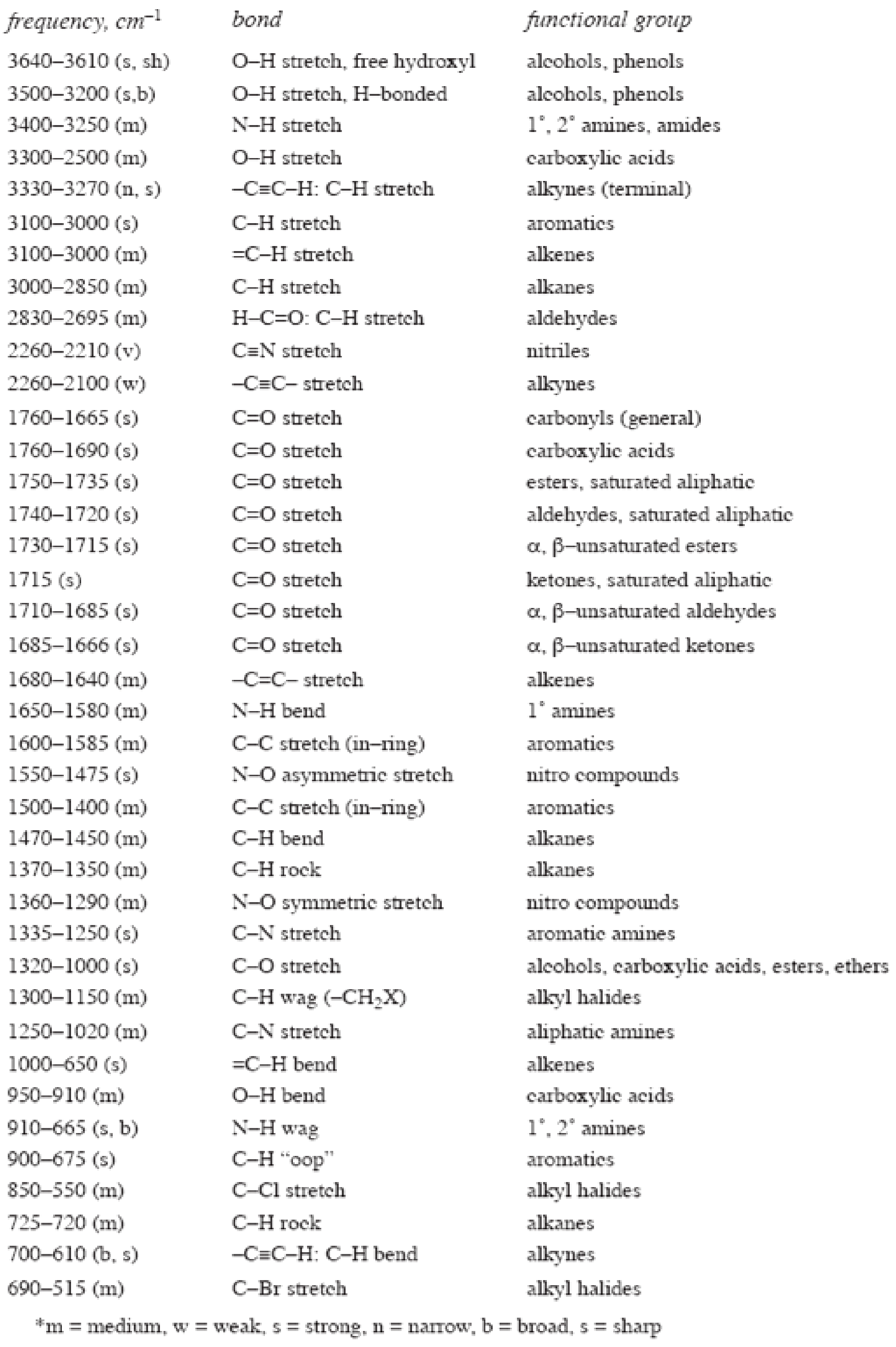
List of Words

GC	Gas Chromatography
FTIR	Fourier Transform Infrared Spectroscopy
CSTR	Continuous Stirrer Tank Reactor
FID	Flame Ionization Detector
TCD	Thermal Conductivity Detectore
PID	Proportional Integral Derivative
Pd/C	Palladium Carbon
Pt	Platinum
RT	Retention Time

Appendices

Appendix 1 Functional Group Frequency Range IR

Table 10 FTIR Identification [23]

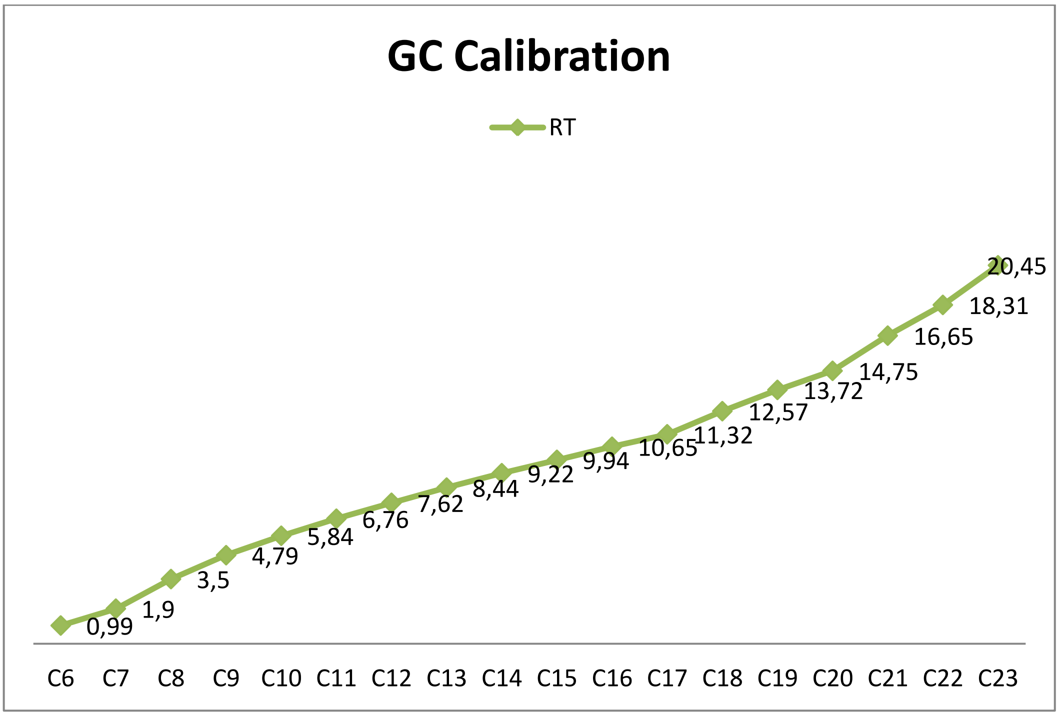


frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1685 (s)	C=O stretch	α, β–unsaturated aldehydes
1685–1666 (s)	C=O stretch	α, β–unsaturated ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

*m = medium, w = weak, s = strong, n = narrow, b = broad, s = sharp

Appendix 2 GC Calibrations

Liquid Sample Calibration



Gas Sample Calibrations

	Compound		**Temp 350 °C**
TCD			
		RT	Area
	Hydrogen	0.95	720837
	CO_2	3.46	359468
		5.61	9340
	Nitrogen	5.81	31493
	Ethene	6.49	114930
	Ethane	7.11	52555
	Methane	7.71	42265
	CO	9.15	302175
FID			
	C_6 Excess	2.04	82115
	Methane	2.86	314734
	Ethane/Ethane	3.16	618892
	Propane/Propene	3.7	4753201
	Butane	4.23	227152
	Butene	4.6	201436
	Pentane	6.3	31063
	Pentene	6.9	15113

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