

Hydrodeoxygenation of Pinyon Juniper Catalytic Pyrolysis Oil to Hydrocarbon Fuels

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Abstract

As a renewable source, biomass is an essential option for diminishing dependence on conventional fossil fuel energy sources. Pyrolysis is a promising technology for the conversion of biomass into liquid fuels. However, several challenges associated with using pyrolysis oils such as their high acidity and low energy content inhibit their direct use as transportation fuels. We conducted a batch hydrodeoxygenation of pinyon juniper catalytic pyrolysis oil using Ni/SiO₂-Al₂O₃ catalyst to improve the following properties of the oil: heating value, acidity, oxygen content, water content, and viscosity. During the hydrogenation process, the influence of four experimental factors; temperature, catalyst loading, residence time, and hydrogen pressure was investigated. Once hydrogenation was completed, gas, coke, and a liquid product of two immiscible phases (aqueous and organic), were obtained. Maximum hydrogenation was obtained at a reaction temperature of 450 °C with catalyst loading of 20% (wt. % of total bio-oil feedstock), an initial hydrogen cold pressure of 1000 psi and a residence time of 30 minutes. At these conditions, bio-oil was deoxygenated by 96.17%. After hydrodeoxygenation, the higher heating value of the organic liquid product was 45.68 MJ/kg compared to 27.64 MJ/kg of the bio-oil. The water content of the organic liquid was zero compared to 1.63% of the bio-oil using Karl Fischer titration method. The aqueous fraction of the liquid product was 99.61% water. Furthermore, pH of the organic liquid was 6.87 compared to 3.46 of the starting material. The viscosity of bio oil was 119.37 cP while it was 1.27 cP for the organic liquid product. The hydrogenation process provided a means of producing upgraded bio-oil, which possessed properties similar to that of gasoline.

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1. Introduction

The global demand for energy is growing due to the development of society. Considering the limited supply of fossil fuels, the need for sustainable renewable fuels is increasing [1]. Fast pyrolysis technique has drawn scientists' attention in recent decades because of its potential to produce liquid fuels. Fast pyrolysis is a thermochemical decomposition process that occurs in absence of oxidizing agents at elevated temperatures [2-5]. This process is highly effective at breaking down macromolecular structures into smaller organic compounds [3]. A number of studies on fast pyrolysis oils of different types of feedstock such as woody and proteinaceous biomasses, grasses, and animal waste have indicated the different properties of the final bio-oil [4-8]. However, their qualities were not suitable for direct refinery due to poor stability, high acidity, and low heating value [9-12].

The high oxygen and water content of bio-oil lowers its heating value. The pH of bio-oil is usually between 2-4 due to the presence of carboxylic acids [13, 14]. The acidic nature of bio-oil causes harsh conditions for the equipment used for transportation, storage, and processing. Another

problem that is associated with bio-oil is stability during storage. The instability of bio-oil is attributed to presence of highly reactive organic compounds causing repolymerization. Moreover, organic acids, aldehydes, and ketones can react to form hemiacetals, acetals, and ethers respectively [15, 16]. Overall the unfavorable properties of pyrolysis oils make it impossible to use as drop-in transportation fuels [17, 19].

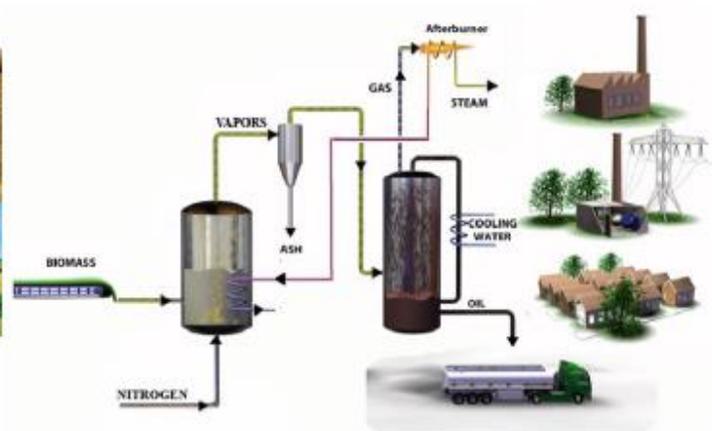
Intensive studies have been carried out on upgrading of pyrolysis oils through different techniques such as esterification under supercritical ethanol, hydrogenation/hydrodeoxygenation (HDO), hydrocracking, emulsification, solvent addition, and steam reforming [17, 19, 20]. Among these techniques, catalytic hydrodeoxygenation of pyrolysis oil is one of the most efficient technologies to improve its fuel quality. In addition to hydrogenation of unsaturated compounds, the majority of hydrogenation catalysts normally favor several other reactions simultaneously such as cracking, decarbonylation, decarboxylation, and hydrodeoxygenation [11, 20-22].

Motivation

Alternative energy



- Bio-oil's negative properties
- What is the solution ?



2. Materials and methods

PJ biomass chips were supplied by the U.S. Bureau of Land Management. Red Mud, supplied by Almatris (Burnside, LA, USA) was used as catalyst for fast pyrolysis of biomass. The wet red mud was dried at room temperature and then ground and sieved to a particle size of 125–180 μm for fluidized-bed pyrolysis. The ground particles were calcined at 550 $^{\circ}\text{C}$ in a muffle furnace (Thermo Scientific, Inc., Waltham, MA) for 5 h before being used for the pyrolysis. The detailed characterization of the red mud has been reported elsewhere [8-10]. Commercial Nickel on silica/alumina (~65 wt % loading Ni) catalyst powder, obtained from Sigma-Aldrich (St. Louis, MO, USA), was used (as received) in HDO experiments. High purity (99%) hydrogen (Airgas, PA, USA) was used for HDO experiments.

The bio-oil was subjected to HDO reactions in a Parr Series 4571 1000 mL autoclave reactor (Parr Instruments, Moline, IL, USA). The reactor can withstand a maximum pressure of 35 MPa at 500 $^{\circ}\text{C}$. A Parr 4848 controller was used to control the internal temperature and impeller speed. In a typical test, bio-oil (30 g) and catalyst (6 g) were loaded into the reactor. The reactor was first flushed with nitrogen three times and then flushed with hydrogen three times to purge the reactor. High purity hydrogen was supplied from a reservoir tank via a pressure regulator. The reactor was then pressurized with hydrogen (3.5, 5.2, 7, 8.6, or 10 MPa) and a gas sample was taken from a gas release valve from the gas sampling port for gas analysis when the reactor was at room temperature. The reactor was then heated to reaction temperature (350, 400, 450, or 500 $^{\circ}\text{C}$) at heating rate of 10 $^{\circ}\text{C}/\text{min}$ using a heating mantle. The reaction time was recorded when the required temperature was reached. The stirrer speed was kept constant (~1000 rpm) in all experiments.

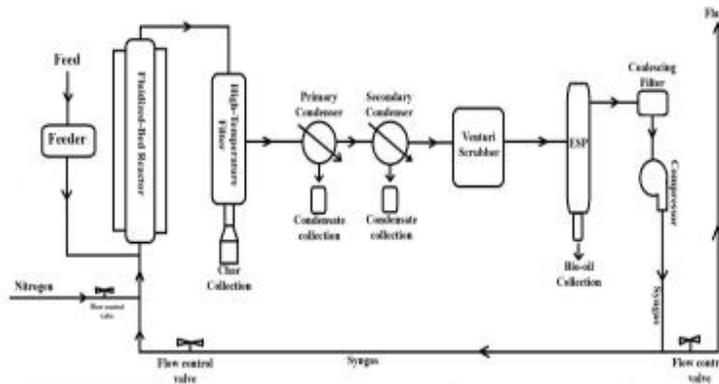
After the desired reaction time (15, 30, 60, or 90 minutes), the reactor was cooled to room temperature using the internal cooling coil and an external air fan simultaneously. A gas sample was collected in a tedlar bag for gas analysis when the reactor was cooled down to room temperature. Hydrogen consumption was measured using equation (1).

$$H_2 \text{ consumption } \left(\frac{\text{moleH}_2}{\text{kg biooil}} \right) = (n_{iH_2} - x_{fH_2} \cdot n_{ftot}) \times \frac{1}{30 \text{ g biooil}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \quad (1)$$

Where n_{iH_2} is the initial number of mole of hydrogen, x_{fH_2} is the final mole fraction of hydrogen, and n_{ftot} is the total number of mole of gas at the end of experiment.

After each experiment, the liquid products were collected in centrifuge test tubes and centrifuged for 30 minutes at g-force of 2147 to separate the resulting aqueous and organic phases and residual solids and catalyst. Both liquid phases were separated and weighed for mass balance computation. The solids (catalyst and coke) were collected and dried at 95 °C for 6 hours. The vessel and reactor parts were rinsed with methanol-toluene mixture (1:1 vol. ratio) to collect any remaining catalyst and oil. The solvent washings were filtered through Watman 42 ashless filter paper (GE Healthcare, UK) and dried at 95 °C. The weight of filter paper was recorded before and after filtration.

Bio-oil Production



Properties	PJ biomass	Catalytic PJ bio-oil
Composition (wt. %)		
Moisture	6.65 ± 0.09	NA**
Ash content	0.53 ± 0.06	0.00
Nitrogen	0.17 ± 0.01	0.47 ± 0.04
Carbon	54.43 ± 0.11	66.88 ± 0.21
Hydrogen	6.27 ± 0.09	7.20 ± 0.07
Sulfur	0.00	0.00
Oxygen	38.60 ± 0.12	25.42 ± 0.12
HHV (MJ/kg)	19.37 ± 0.11	27.64 ± 0.23
pH	NA**	3.46 ± 0.05
Water content (wt. %)	NA**	1.63 ± 0.08
Density (g/cm ³)	0.55 ± 0.03	1.16 ± 0.02
Dynamic viscosity (cP)	NA**	119.37 ± 5.43
* By difference		
** Not applicable		



Catalytic Pyrolysis



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Experimental

Experimental parameters:

T= Temperature (°C) – four levels (350, 400, 450, 500)

C%= Catalyst loading (wt. % of feed bio-oil) – four levels (10, 15, 20, 25)

P_{H2}= Initial hydrogen pressure (MPa) – five levels (3.5, 5.2, 7, 8.6, 10)

RT= Residence time (min) – four levels (15, 30, 60, 90)

$$Y_{liquid}(\%) = \frac{W_l}{W_f} \times 100$$

$$Y_{gas}(\%) = \frac{W_g}{W_f} \times 100$$

$$Y_{coke}(\%) = \frac{(W_s - W_c)}{W_f} \times 100$$

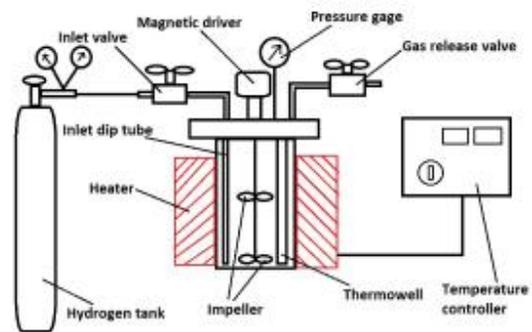
W_l = mass of liquid

W_g = mass of gas

W_f = total mass of feed biomass and consumed hydrogen

W_s = mass of solid residue

W_c = mass of catalyst



Hydrodeoxygenation (HDO)

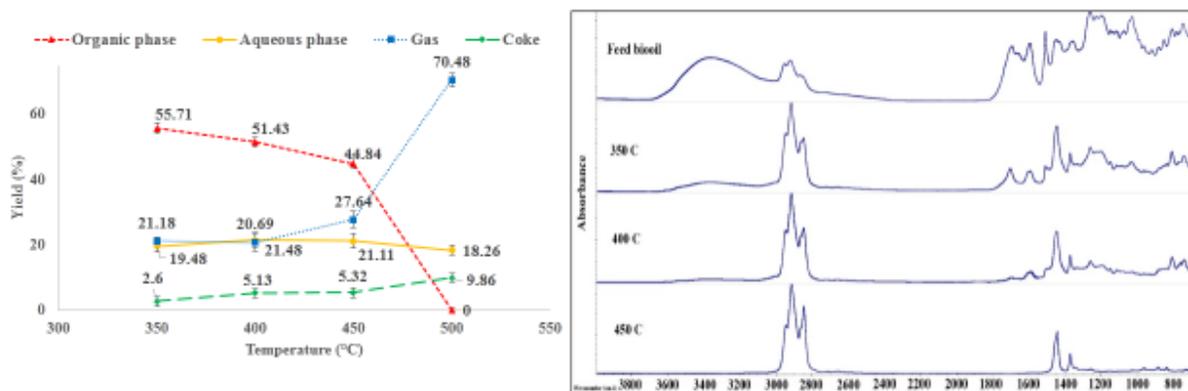


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3. Results and discussion

The influence of four experimental factors; temperature, pressure, catalyst loading, and reaction time on physicochemical properties of HDO oil and products yield distribution are presented in this section.

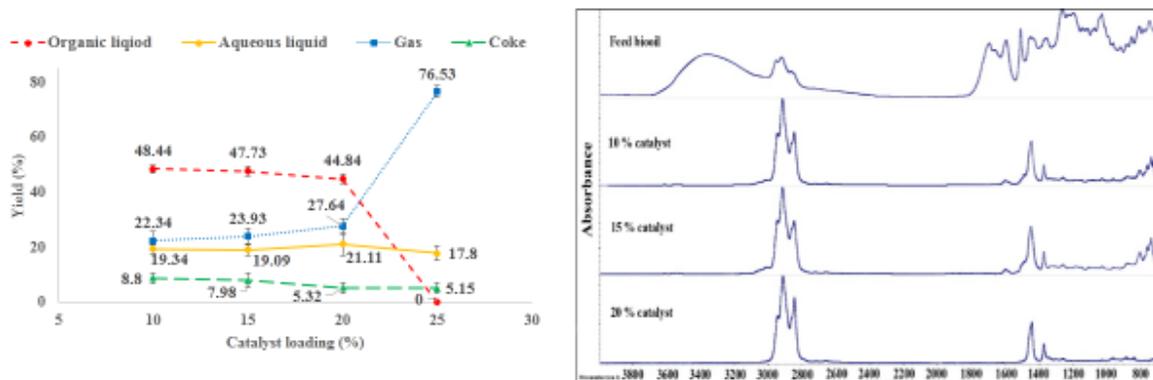
Temperature Effect



Properties	C%, P _{H₂} , and RT fixed at 20%, 7 MPa, and 60 min respectively			
	350 °C	400 °C	450 °C	500 °C
H ₂ consumption (mole/kg bio-oil)	48.12 ± 0.89	50.33 ± 0.77	57.2 ± 1.23	90.81 ± 1.68
HHV (MJ/kg)	42.07 ± 0.67	42.57 ± 0.91	45.44 ± 0.84	...
pH	5.72 ± 0.33	6.53 ± 0.21	NA	...
Water content (wt. %)				
Organic liquid	<MDL*	<MDL*	<MDL*	...
Aqueous liquid	98.87 ± 0.85	97.15 ± 0.45	98.05 ± 1.05	...
Density (g/cm ³)	0.88 ± 0.02	0.84 ± 0.02	0.79 ± 0.01	...
Dynamic viscosity (cP)	3.22 ± 0.01	1.58 ± 0.01	1.35 ± 0.01	...

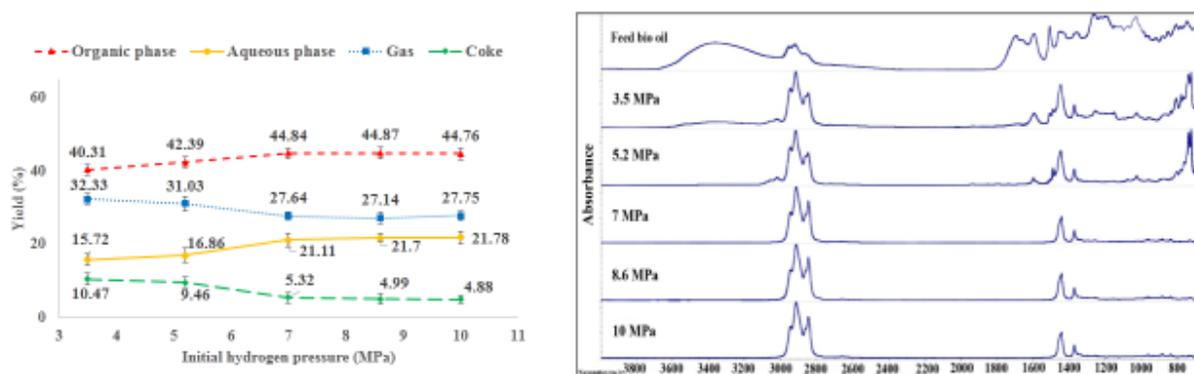
* The method detection limit was 0.05%.

Catalyst Loading Effect



Properties	T, P _{H₂} , and RT fixed at 450 °C, 7 MPa, and 60 min respectively			
	10%	15%	20%	25%
H ₂ consumption (mole/kg bio-oil)	44.44 ± 1.02	54.38 ± 1.14	57.20 ± 1.23	92.07 ± 1.23
HHV (MJ/kg)	43.21 ± 0.94	44.16 ± 0.61	45.44 ± 0.84	...
pH	6.43 ± 0.16	6.53 ± 0.11	NA	...
Water content (wt. %)				
Organic liquid	<MDL	<MDL	<MDL	...
Aqueous liquid	98.51 ± 0.15	99.18 ± 1.05	98.05 ± 0.95	98.54 ± 1.15
Density (g/cm ³)	0.86 ± 0.02	0.84 ± 0.04	0.79 ± 0.01	...
Dynamic viscosity (cP)	1.97 ± 0.04	1.08 ± 0.03	1.35 ± 0.01	...

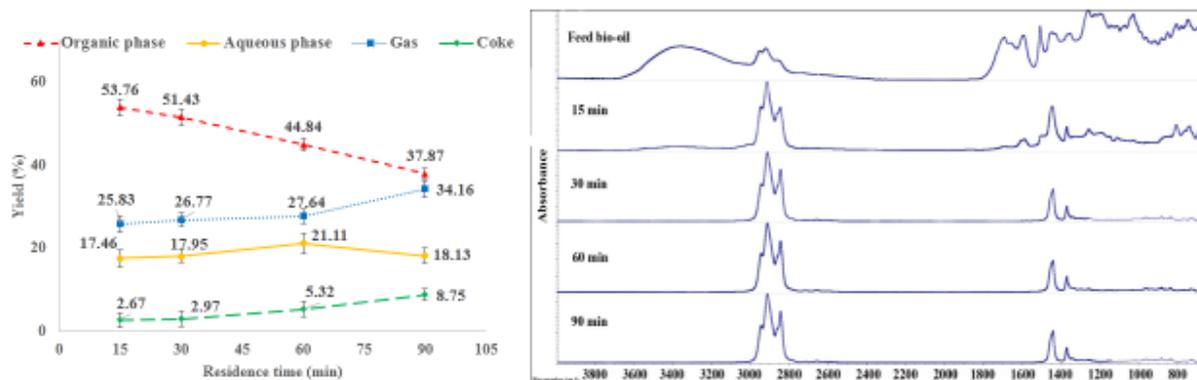
Hydrogen Pressure Effect



Properties	T_r , C%, RT fixed at 450 °C, 20% and 60 min respectively				
	3.5 MPa	5.2 MPa	7 MPa	8.6 MPa	10 MPa
H_2 consumption (mole/kg bio-oil)	43.11 ± 0.34	47.89 ± 0.29	57.2 ± 1.23	57.21 ± 1.02	57.28 ± 0.97
HHV (MJ/kg)	42.72 ± 1.04	43.14 ± 0.56	45.44 ± 0.84	45.56 ± 0.65	45.37 ± 0.24
pH	4.88 ± 0.03	5.16 ± 0.03	NA	NA	NA
Water content (wt. %)					
Organic liquid	1.07 ± 0.05	0.73 ± 0.05	<MDL	<MDL	<MDL
Aqueous liquid	94.77 ± 0.95	95.36 ± 0.65	98.99 ± 1.15	97.12 ± 1.15	
Density (g/cm ³)	0.88 ± 0.02	0.85 ± 0.01	0.79 ± 0.01	0.81 ± 0.01	0.81 ± 0.02
Dynamic viscosity (cP)	1.54 ± 0.02	1.41 ± 0.01	1.35 ± 0.01	1.27 ± 0.02	1.26 ± 0.01

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Residence Time Effect

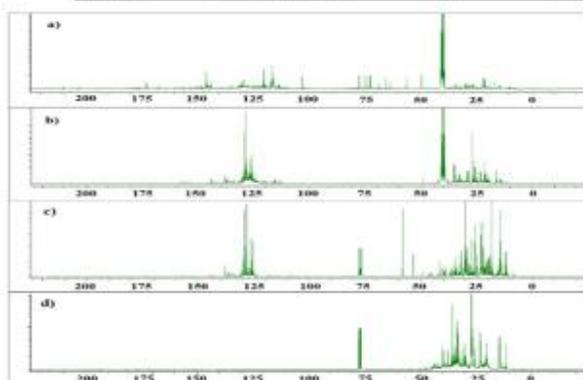


Properties	T_r , C%, and P_{H_2} fixed at 450 °C, 20 %, and 7 MPa respectively			
	15 min	30 min	60 min	90 min
H_2 consumption (mole/kg bio-oil)	46.12 ± 0.38	49.85 ± 0.51	57.20 ± 1.23	60.18 ± 1.05
HHV (MJ/kg)	43.27 ± 0.44	45.58 ± 0.48	45.44 ± 0.84	45.81 ± 0.67
pH	6.19 ± 0.03	NA	NA	NA
Water content (wt. %)				
Organic liquid	0.73 ± 0.05	<MDL	<MDL	<MDL
Aqueous liquid	95.29 ± 0.75	99.61 ± 0.75	98.05 ± 1.05	98.56 ± 1.35
Density (g/cm ³)	0.85 ± 0.01	0.81 ± 0.01	0.79 ± 0.01	0.81 ± 0.02
Dynamic viscosity (cP)	1.27 ± 0.03	1.26 ± 0.02	1.35 ± 0.01	1.11 ± 0.01

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¹³C NMR Analysis

Chemical shift region (ppm)	Dominant type of carbon	Percentage of carbon based on ¹³ C NMR analysis			
		Feed bio-oil (a)	HDO oil-400 °C (b)	Commercial gasoline (c)	HDO oil-450 °C (d)
0-28	saturated aliphatic groups	16.9	42.9	48.3	61.2
28-55	unsaturated aliphatic groups	10.6	16.7	13.3	38.8
55-95	alcohols, ethers, phenolic methoxys, anhydrosugars	13.1	0	1.7	0
95-165	aromatics, furans	56.7	40.4	36.7	0
165-180	organic (carboxylic) acids, esters	1.6	0	0	0
180-215	ketones, aldehydes	1.1	0	0	0



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4. Conclusion

A parametric hydrodeoxygenation study using commercial Ni/SiO₂-Al₂O₃ catalyst was carried out on pyrolysis oil derived from Pinyon Juniper. HDO experiments resulted in conversion of the bio-oil into two liquid phases (aqueous and organic), as well as gas and coke. The mass balance analysis of HDO experiments demonstrated that product yield distributions were considerably influenced by temperature, hydrogen pressure, and reaction time. High temperature lead to high catalytic activity for HDO. Hydration reactions mainly occurred at low temperature, while deoxygenation or cracking of oxygenated compounds were predominant at high temperature. With increasing reaction temperature from 350 °C to 450 °C the yield of upgraded oil decreased, but it was beneficial in improving the physicochemical properties. At low hydrogen pressure, hydrogenation dominated deoxygenation reactions. With increase in hydrogen initial pressure, deoxygenation reactions were favored, in addition to hydrogenation. The increase in reaction time led to the decrease in organic liquid yield, due to the formation of gas-phase components and coke

through cracking and polymerization respectively. The properties of HDO oils were significantly improved compared to the original bio-oil. This work provided a new alternative for production of liquid hydrocarbon from bio-oil.

Conclusion

- Increasing the reaction temperature decreased the organic liquid yield but it was beneficial in improving the physicochemical properties.
- Presence of suitable amount of catalyst prevented unfavorable reactions.
- With an increase in initial hydrogen pressure, deoxygenation reactions were favored in addition to hydrogenation.
- Increasing the residence time led to decreases in organic liquid yield due to gas and coke formation.
- Major challenges were carbon loss due to coke and gas formation. Also H₂ consumption adds to the cost of operation.

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Acknowledgement

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