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EFFECT OF PARAMETERS ON PROPYLENE PRODUCTION IN FCC UNIT

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Abstract
This paper deals with the simulation of the Fluid Catalytic Cracking unit for the production of propylene. Propylene, often called "The Crown Prince of Petrochemicals", is the second most important starting product in the petrochemical industry whose demand has been constantly increasing for the last few years. With the constantly rising demand, operators of FCC units look more towards the petrochemicals production to make better their revenues by taking benefit of economic opportunities that arise in the market. Steam crackers and FCC units are the two important sources of propylene in the refinery. There is a shortage in the supply of propylene from the modern steam crackers, which are now producing relatively less propylene. Further, Fluid Catalytic Cracking (FCC) is a process, which is flexible to various reaction conditions, which makes the unit one of the possible means to bridge the gap between the supply and demand of propylene. In this work, a simulation of the FCC unit for the production of propylene was performed in the Aspen HYSYS v10 software tool. Vacuum gas oil imported from the FCC feed library, Atmospheric gas oil, and Naphtha from the atmospheric distillation unit were used as feed to the FCC unit with af3 as the catalyst. Peng-Robinson model was chosen in the fluid package to represent the phase equilibrium behaviour and energy levels of pure components and mixtures because of its superiority in handling hypothetical components (pseudo-components). Simulation of the atmospheric distillation was also carried out to find out the composition of the feed that would enter the riser reactor and then, the FCC unit was simulated to get the final yield of propylene. Later, the effect of parameters like the reactor temperature, catalyst to oil ratio, feed temperature, and amount of ZSM-5 additive on the yield of propylene was studied.

Keywords: Propylene, Aspen HYSYS v10, Atmospheric gas oil, Fluid Catalytic Cracking, Peng-Robinson model,

1. Introduction

The fluid catalytic cracking (FCC) unit is that the hydrocarbon conversion unit within the trendy oil refinery. It uses heat and catalyst to convert a range of high mass feeds (for instance, gas oils, cracked gas oils, deasphalted gas oils, and atmospheric/vacuum resides) into lighter, more valuable products such as gasoline, light fuel oil, and petrochemical feed-stocks such as propylene and butylenes [1]. The fluid catalytic cracking (FCC) unit is the heart of the refinery and has been in operation for over 60 years during which a lot of developments have occurred [2, 3].

Light olefins are building blocks for several end products, such as polyethylene and polypropylene. Recently, the demand for propylene is outpacing that of ethylene and therefore the current provide cannot match the demand. An oversized proportion of propylene is made by steam cracking of light naphtha and during the fluid catalytic cracking process [2, 3].

Propylene demand, as observed from 2009 to 2014, has grown more rapidly than that of ethylene. There are some on-purpose propylene production processes, such as propane dehydrogenation, olefin conversion technology, methanol to propylene process, metathesis, available to sustain the demand of propylene. All these processes have seen only some degree of applicability. Currently, fluid catalytic cracking (FCC) units are serving as the second most important resource for propylene production. With the continually rising demand, operators of FCC units look all the time more to the petrochemicals market to enhance their revenues by taking advantage of economic opportunities that come up in the propylene market. The figure 1 illustrates the global propylene capacity and its demand in million metric tons per year.

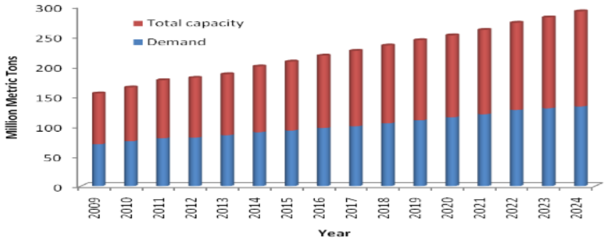

Figure 1: Global propylene capacity and demand
(Source: HIS)

2. Flexibility of FCC for Propylene

Propylene is available in fuel gas and LPG products of the FCC units. It is estimated that 1 million tons of capacity conventional FCC unit of Indian refineries would produce 25-31 tons per annum of propylene depending on the catalyst and process conditions [4].

Reconfiguration of the FCC unit can be done and some of the technologies can be adopted [3, 4]. This aids in maximizing the production of propylene and light olefins. Further, use of catalyst provides an alternative path with the low activation energy for the cracking reactions. Due to the lower activation energy, the C–C bond split requires less energy. So there is a possibility of obtaining energy savings and flexibility of operation. Although Steam cracking is the primary source of propylene, the shift of the feedstock from heavier petroleum fractions like Naphtha to lighter ones like ethane has resulted in the decrease of propylene yield and producing more and more ethylene. So the FCC process became an alternative route to Steam Cracking. Accordingly, the temperatures for the steam cracking process of Naphtha are 150-250^{0}C higher than that of catalytic cracking of Naphtha. The catalyst in the FCC process has the advantage of improving selectivity to target products. So it is easy to shift the production towards desired products such as propylene. Even if the same operating conditions were kept for Steam cracking and catalytic cracking, the yield of light olefins from FCC would still be increased by at least 15 % than that of the SC process.

Due to the fastest-growing propylene demand, the propylene demand from FCC is also increasing. However, the global FCC capacity is lagging behind. Therefore, to sustain with the demand, propylene yields from FCC need to be enhanced. FCC units in use today are of two basic types (Stacked and side by side configurations) based on the arrangement of the reactor and regenerator [1] is as shown in Figure 2.

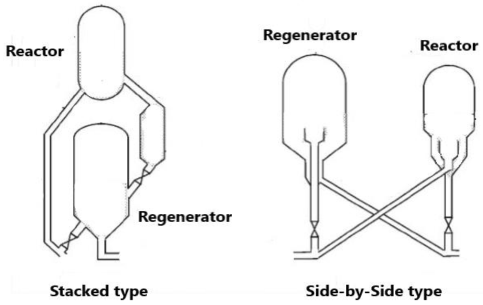

Figure 2: FCC type configuration

The 'side-by-Side' type is one in which the reactor and regenerator are separate vessels adjacent to each other. The Stacked or Ortho-flow type reactor is mounted on the top of the regenerator [5]. To achieve the challenging propylene yields required to meet the growing demand for propylene from FCC, refiners are making several modifications to the unit. All the modifications made can be put together and classified into two types: Riser (Up flow) and Downer (Down flow) technologies [6] as shown in Figure 3.

2.1 Riser FCC Technology

Deep catalytic cracking (DCC) and catalytic pyrolysis process (CPP) are the two technologies come under the category of the processes, which operate using Riser FCC technology principles. These are developed by SINOPEC.

Deep Catalytic Cracking (DCC): DCC is a process, which is derived from the conventional FCC process. Its flow sheet is similar to FCC and consists of a continuous reactor and regenerator system with the circulation of fluidized catalyst. The high reactor temperature is maintained compared to the conventional process so that a high olefin yield can be achieved [7, 8].

Catalytic Pyrolysis Process (CPP)**:** CPP is further modified from DCC and the modification includes new catalyst formulation, varied operating conditions and some changes in engineering. CPP uses a riser reactor, a quenching technology and a crosscurrent degassing device to minimize the flue gas adsorbed and entrained by the regenerated catalyst [8, 9].

2.2 Downer FCC Technology

High Severity Fluid Catalytic Cracking (HS–FCC): The HS–FCC process is a process which is operated under considerably higher operating temperatures (550–650^{0}C) than that of conventional FCC units [10]. The primary objective is to increase production of propylene and gasoline with high octane numbers. Short residence time can be achieved by separating the catalyst and the products immediately at the reactor outlet. For this purpose, a high productiveness short residence time product separator has been developed and is capable of suppressing side reactions.

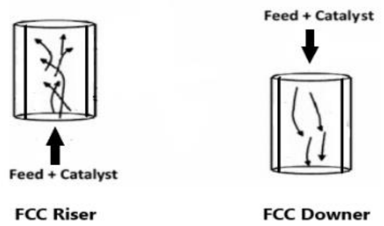

Figure 3**:** Illustration of flow in riser and downer FCC

The design and operation of an FCC unit are also affected by the type of catalyst used in the process [11]. The desired properties of the catalyst for the conventional FCC process are [2]:

- Good stability so that it can sustain high temperatures and steam.
- High activity to carry out the conversion of the feed without the intervention of a considerable amount of thermal cracking.
- Large pore sizes to crack high molecular weight molecules.
- Low coke production so the activity of the catalyst can remain active for a longer time.

3. Process Details

The process flow diagram of the FCC unit side by side configured is as shown in figure 4. The reactor and the regenerator are the two most important components of the basic process FCC. All the main processes that take place in the FCC process are Preheat system; Riser/Reactor; Regenerator; Fractionator; Flue gas system, and Catalyst handling system.

The Gas Oil feed before entering into the reactor is sent to the feed preheat system and gets preheated to the temperature of about 500-700^{0}F [5]. The preheated feed then enters into the riser

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where it gets mixed with the hot regenerated catalyst. The heat from the catalyst vaporizes the feed to the required temperature for the cracking reactions to occur. Hence, the cracking reaction sets in the riser and the mixture of catalyst and hydrocarbon vapor travels up the riser into the reactor, which acts as a separation vessel or disengagement vessel. Initiation of the cracking reaction takes place in the riser when the feed gets contacted with the hot catalyst and terminates when oil vapors are separated from the catalyst in the reactor separator.

After the separation of the vapors from the catalyst, the spent catalyst is then sent to the regenerator, which restores the activity of the catalyst. The deposition of coke takes place during the cracking reactions on the surface of the catalyst as a result of which its activity will be reduced. Therefore, there is a need for restoration of its activity by removing the coke deposited on its surface. So air is supplied to the regenerator by a large air blower to reactivate the catalyst. High speed of air is maintained within the regenerator to stay the catalyst bed within the fluidized state. Then the air is sent to the regenerator through the distributor at the bottom. The combustion of the coke takes place inside the regenerator as the air burns off the coke. Since the combustion reaction is exothermic, heat is produced during the process. This heat is supplied by the regenerated catalyst in the form of sensible heat to the reactor and is used in the catalytic cracking process, which is endothermic. Some amount of flue gas produced during combustion process inside the regenerator is passed through the cyclone separator, which recovers the residual catalyst.

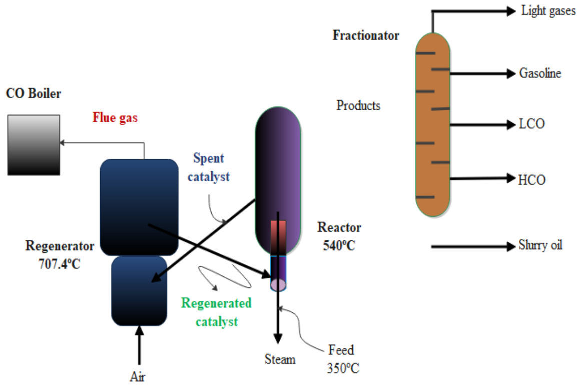

Figure 4: Flow Diagram of Fluid Catalytic Cracking

The products from the reactor free from the spent catalyst particles are sent to the fractionator, which de-superheats and recovers different products from the reactor effluent vapors. Condensation and re-vaporization of hydrocarbon components take place as the vapor flows upward through trays in the tower to accomplish fractionation near the base. Slurry or decant oil which is the bottom product from the main column is sent to the slurry settler and clarified slurry is recovered. Heavy Cycle Oil (HCO), Light Cycle Oil (LCO), Gasoline are other products obtained above the bottoms. At the top of the column, the light gases flow as vapors and are obtained. These light gases constitute lighter gases like methane, ethane, about 95% C_3, C_4, and about 10% naphtha.

4. Simulation of the FCC unit

The Simulation of the FCC plant has been executed using a commercial software tool, Aspen HYSYS Petroleum Refining from Aspen Technology, Inc. Simulation software enables the operation of the whole process so that the faults of designs in real process equipment and adjustment of flow rates of process streams in the plant can be identified without being actually running the real plant.

Data from 800,000 tons per year feed capacity commercial FCC plant located in the Asia Pacific is used and the methodology to simulate the fluid catalytic cracking (FCC) process is demonstrated [12]. Precise predictions of yields of products and their properties can be obtained by giving operating conditions and feed input parameters. Aspen HYSYS simulator ensures the feasibility of a process. The effect of various operating conditions on various reactions and product yields can be studied. It is a well-built means for simulation studies and with this, analysis of a process outcome can be done effectively. A High degree of litheness is also offered by HYSYS because there are numerous ways to carry out specific tasks. HYSYS is an exceptionally handy process simulation tool with the capabilities like flexibility, consistency, and logical approach.

The following three major aspects of its design mark the to the usability of HYSYS:

- Event Driven operation
- Modular Operations
- Multi-flow sheet Architecture

The sequence of actions after selecting a new case in Aspen HYSYS is as follows: Select File > New > Case. Then the predetermined set of components for the FCC model are imported by navigating to the directory location, "C:\Program Files\Aspen Tech\Aspen HYSYS" and clicking 'Import'. "FCC components celsius.cml" is selected and it appears as the component list.

After the addition of components, 'Fluid Package' is selected by moving to the 'Fluid Packages' tab in the Simulation Basis Manager and clicking 'Add'. It refers to the thermodynamic system related to the chosen list of components. Then, the process model is built by clicking on the 'Enter Simulation Environment'. From the Reactors palette, the FCC icon is selected and a new unit is configured by determining the required dimensions. The details of the input feed must be specified after the completion of the basic FCC configuration. This is done by selecting feed data and importing vacuum gas oil feed "fccfeed_vgo.csv" from the feed library. In a similar manner, the catalyst is imported from the FCC catalyst library. The catalyst used in this model is "af-3". The catalyst blend and catalyst activity data are entered. 800,000 tons i.e., 18 MBPD of Vacuum Gas Oil [12] is fed to the unit. The feed characterization of VGO feed is shown in table 1.

Table 1: Characteristics of VGO feed

Feed	Flow rate (kg/hr)	Specific gravity	Distillation Type	Initial Point (^{0}C)	5%	10%	30%	50%
Vacuum gas Oil	108208	0.9	D-1160	269.0	358.6	376.4	419.0	452.3
Feed	70%	90%	95%	End Point	Nitrogen (ppm wt)	Sulfur (wt.%)	CCR (wt. %)	Vanadium (ppm wt)
Vacuum gas Oil	488.0	541.8	567.9	665.8	2409.0	0.56	1.86	0.3
Feed	Nickel (ppm wt)	Sodium (ppm wt)	Iron (ppm wt)	Copper (ppm wt)	Olefins (Liq. vol.%)	Naphthenes (Liq. vol.%)	Aromatics (Liq. vol.%)	
Vacuum gas Oil	3	0.3	2.1	0.1	28.5	8.529	23.6	

Besides VGO feed, 18 MBPD of Atmospheric Gas oil (AGO) and Naphtha from the atmospheric distillation unit are fed to the FCC unit and simulation is carried out. To obtain the feed composition, simulation of the atmospheric distillation unit (ADU) is also done by processing 100 MBPD of crude oil. Assay data shown in table 2 is used to characterize the crude oil and table 3 shows the composition of atmospheric gas oil obtained from the simulation of ADU. The operating conditions maintained are the feed temperature is 350^{0}C, reactor temperature is 540^{0}C, reactor pressure is 1.8 bar, regenerator temperature is 707^{0}C, regenerator pressure is 2.5 bar, and the air temperature is 200^{0}C.

Table 2: Crude assay

Assay Liquid Volume %	0.0	4.5	9.0	14.5	20.0	30.0	40.0
Boiling Temperature (°F)	15.0	90.0	165.0	240.0	310.0	435.0	524.0
Assay Liquid Volume %	50.0	60.0	70.0	76.0	80.0	85.0	Std. Density
Boiling Temperature (°F)	620.0	740.0	885.0	969.0	1015.0	1050.0	29.32°API
Light Ends	Methane	Ethane	Propane	i-Butane	n-Butane	H_2O	
Liquid Volume %	0.0065	0.0225	0.3200	0.2400	0.8200	0.0000	

Table 3: Composition of Atmospheric Gas Oil

Component	H_2O	NBP[0]179*	NBP[0]199*	NBP[0]219*	NBP[0]239*	NBP[0]258*
Liquid vol. fraction	0.0004	0.0001	0.0003	0.0009	0.0029	0.0075
Component	NBP[0]278*	NBP[0]298*	NBP[0]318*	NBP[0]338*	NBP[0]357*	NBP[0]377*
Liquid vol. fraction	0.0157	0.0305	0.0552	0.0968	0.1721	0.2476
Component	NBP[0]397*	NBP[0]417*	NBP[0]445*		NBP[0]483*	
Liquid vol. fraction	0.2199	0.1268	0.0232		0.0001	

The composition of naphtha obtained from the atmospheric distillation of crude oil is presented in table 4, and The equilibrium catalyst properties are as shown in table 5.

Table 4: Composition of Naphtha

Component	H_2O	Methane	Ethane	Propane	i-Butane	NBP[0]1*
Liquid vol. fraction	0.0001	0.0003	0.0010	0.0139	0.0104	0.0943
Component	NBP[0]20*	NBP[0]40*	NBP[0]60*	NBP[0]80*	NBP[0]100*	NBP[0]120*
Liquid vol. fraction	0.0911	0.0906	0.0932	0.1051	0.1150	0.1181
Component	NBP[0]139*	NBP[0]159*	NBP[0]179*		NBP[0]199*	
Liquid vol. fraction	0.1167	0.1046	0.0440		0.0017	

Table 5: Equilibrium catalyst properties

Metal content (ppm wt)	Value
V	5000
Ni	4044
Na	3103
Fe	5553
Cu	57
Equilibrium activity (%)	66

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Inventory (kg)	150000
ZSM-5 additive per unit mass of base blend	0.2

The process flow diagram of the FCC Simulation unit with different feeds are depicted in figures 5 and 6. The flow sheet of FCC plant with Naphtha feed is also similar to the one with AGO feed. Here, Naphtha cut from the atmospheric column is sent to the FCC reactor.

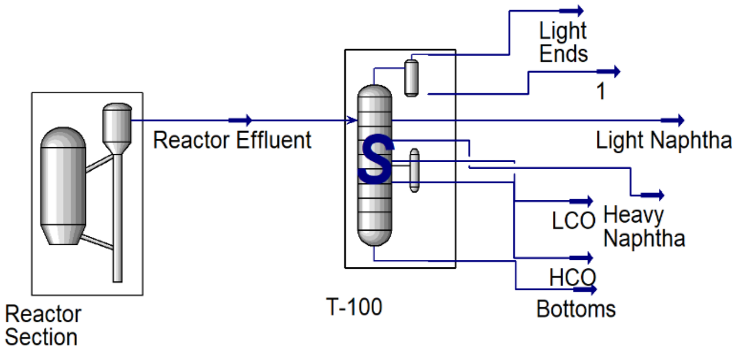

Figure 5: Flow sheet of simulation of FCC plant

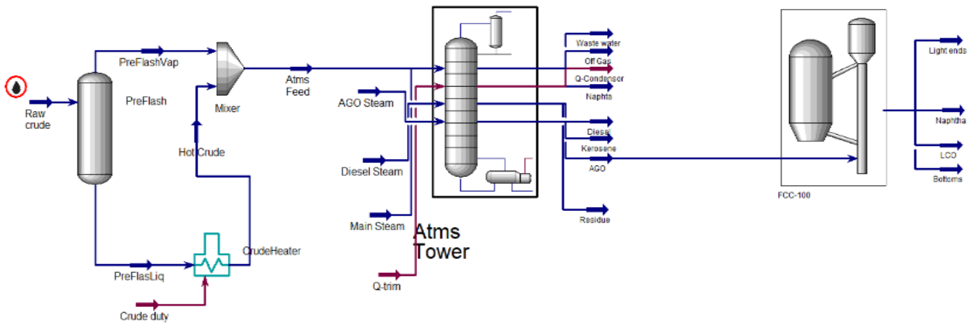

Figure 6: Flow sheet of simulation of FCC plant with AGO as feed

5. Results and Discussions

Since propylene is our required product from the unit, the effect of various parameters like feed temperature, rector temperature, amount of ZSM-5 additive, the catalyst to oil ratio, are studied. This is done by varying the parameter and noting down the propylene mass flow rate at the corresponding value.

5.1 Effect of ZSM-5 additive on propylene production:

For the purpose of producing more propylene and olefins, more ZSM-5 is being used as the main active component of the catalyst in the FCC unit [13]. The critical value of ZSM-5 amount is 0.23 for VGO feed, 0.39 for AGO feed and 0.59 for Naphtha feed. It was observed that increasing the amount of ZSM-increases the production of propylene [14] as depicted in figure 7.

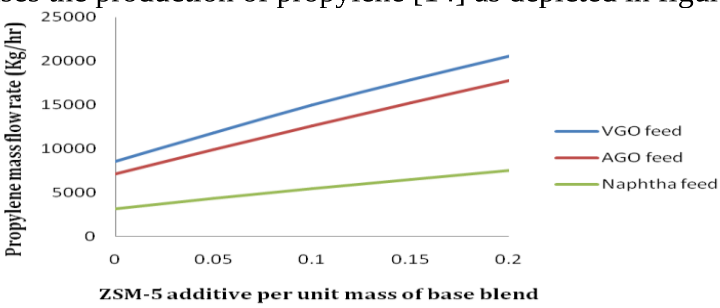

Figure 7: Plot of ZSM- 5 Additive vs Propylene mass flow rate for VGO feed

The critical value of ZSM-5 amount and the corresponding propylene mass flow rate for three feeds are as shown in table 6.

Table 6: Propylene mass flow rate at critical values of ZSM-5 additive

Feed	ZSM-5 additive per unit mass of base blend	Propylene mass flow rate (Kg/hr)
Vacuum Gas Oil	0.23	23964.0
Atmospheric Gas Oil	0.39	26292.1
Naphtha	0.59	12771.2

5.2 Effect of feed temperature on propylene production:

A rise in feed temperature will decrease the catalyst circulation rate to keep reactor outlet temperature constant. So as the temperature goes up, the amount of propylene produced decreases. The optimum feed temperature ranges at which the system is converged at the given conditions is 180^0C-350^0C. The effect of the temperature of the feed on the production of propylene is as shown in figure 8.

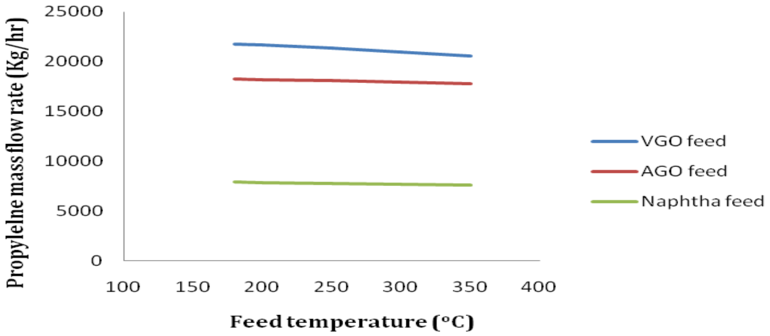

Figure 8: Plot of Feed temperature vs Propylene mass flow rate

5.3 Effect of reactor temperature on propylene production:

As the reactor temperature increases, the amount of propylene increases due to an increase in catalyst circulation rate, which leads to more, cracking. The optimum reactor temperature ranges at which the system is converged at the given conditions is 510-550^0C. The effect of the reactor temperature is shown in figure 9.

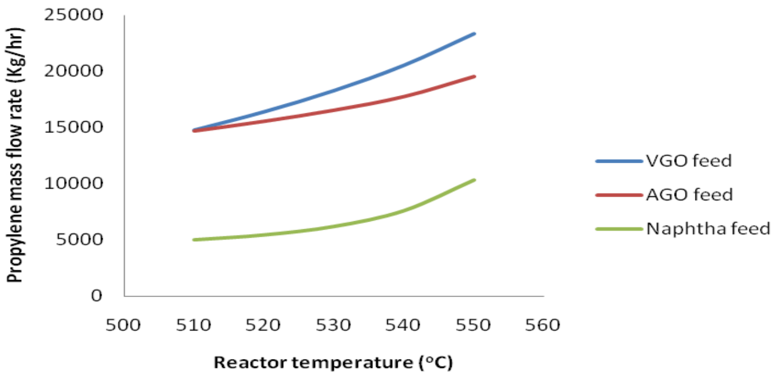

Figure 9: Plot of reactor temperature vs Propylene mass flow rate

5.4 Effect of feed type on propylene production:

The production of propylene requires a disproportionate share of the hydrogen and co-products, including propane, and dry gas requires an even greater share of hydrogen [3]. Therefore, the potential of the propylene production can be limited by the amount of hydrogen available from the feedstock.

A refinery yield is delineated as the % of finished product produced from inputs of crude oil and net unfinished oils. It is calculated by dividing the addition of crude oil and net unfinished inputs into the individual net production of the finished product. The yield of propylene from different feeds operating at the same conditions i.e., at the feed flow rate of 18 MBPD, feed temperature of 350^{0}C, reactor temperature of 540^{0}C, is 15.4 wt% from VGO feed, 11.5 wt% from AGO, and 5.69 wt% from Naphtha feed. The term conversion is to define the percentage of feed that is converted into products inside a unit process. The conversion is 64.13 wt% from VGO, 70.17 wt% from AGO, and 89.61 wt% from Naphtha feed. The yield of other products and conversion are illustrating in table 7.

5.5 Effect of reactor temperature on propylene to ethylene ratio:

The optimum reactor temperature ranges at which the system is converged at the given conditions is 510-550^{0}C [15]. The effect of reactor temperature on propylene to ethylene ratio for different feeds is displayed in figure 10.

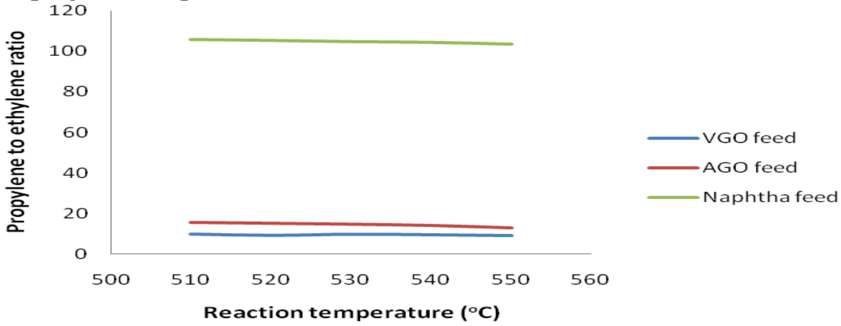

Figure 10: Effect of reactor temperature on propylene to ethylene ratio

5.6 Effect of catalyst to oil ratio on propylene production:

A high C/O ratio will operate to maximize conversion, which tends to favor light olefin production [16]. An increase in the amount of propylene produced with the catalyst to oil ratio with VGO feed is as delineated in figure 11.

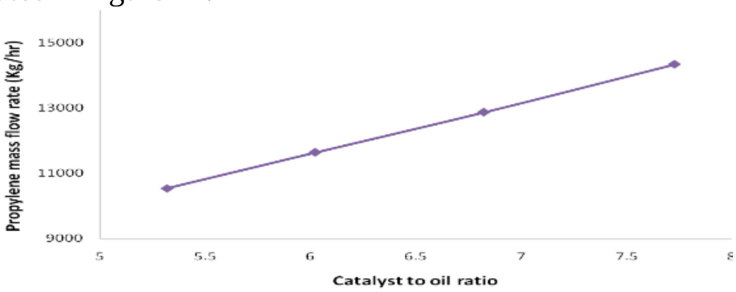

Figure 11: Plot of Catalyst to oil ratio vs Propylene mass flow rate

Table 7: Product yields from different feeds

Product yields	**VGO feed**		**AGO feed**		**Naphtha feed**	
	Mass flow (kg/hr)	**Wt%**	**Mass flow (kg/hr)**	**Wt%**	**Mass flow (kg/hr)**	**Wt%**
H_2S	502	0.32	602	0.39	723	0.53
Fuel Gas	8192	5.27	4539	2.94	572	0.42
Propane	6167	3.97	3179	2.06	98	0.07
Propylene	23964	15.4	17763	11.5	7632	5.69
n-Butane	2533	1.63	2134	1.38	1323	0.98
i-Butane	8917	5.74	6655	4.32	3212	2.39
Butenes	20037	12.9	15841	10.2	8603	6.42

Naphtha C5-430F	25543	16.4	52881	34.3	97131	72.5
LCO 430-650F	26572	17.1	29874	19.4	8160	6.09
Bottoms 650F +	29102	18.7	16020	10.4	5746	4.29
Coke Yield	3691	2.37	4400	2.85	1876	1.40
Total	155223	100	153893	100	133935	100
Conversion (%)	--	64.13	--	70.17	--	89.61

6. Conclusion

The gap between the supply and demand of propylene can be bridged easily by using FCC unit. Simulation of the FCC unit for production of propylene is done by processing 18MBPD of Vacuum gas oil, and propylene yield is 15.4 wt.% from VGO feed, 11.5 wt.% from AGO and 5.69 wt% from Naphtha feed. The effect of different parameters like feed type, feed temperature, reactor temperature and catalyst to oil ratio on the propylene production has been studied. The most interesting phenomenon is the variation of propylene yield with ZSM-5 additive. It is observed that increase in the amount of ZSM-5 additive increases the production of light olefins and hence the production of propylene.

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