



## INTEGRATING REFINING AND PETROCHEMICALS FEEDSTOCKS THROUGH A NOVEL FCC PROCESS

A. Ma'adhah<sup>1</sup>, T. Ino<sup>2</sup>, H. Redhwi<sup>1</sup>, M. Abul-Hamayel<sup>3</sup>, A. Aitani<sup>4</sup>, M. Saeed<sup>5</sup>,  
and A. Maghrabi<sup>6</sup>

1: Professor, Department of Chemical Engineering, KFUPM.

2: Research Scientist, Japan Cooperation Center, Petroleum.

3: Associate Professor, Department of Chemical Engineering, KFUPM.

4: Research Scientist, Center for Refining & Petrochemicals, KFUPM-RI.

5: Engineer I, Center for Refining & Petrochemicals, KFUPM-RI.

6: Researcher, Center for Refining & Petrochemicals, KFUPM-RI.

Correspondence Address: King Fahd University of Petroleum & Minerals  
KFUPM Box 83, Dhahran 31261, Saudi Arabia

Email [amaadhah@kfupm.edu.sa](mailto:amaadhah@kfupm.edu.sa)

Phone (03) 860-3882, Fax (03) 860-4509

### ABSTRACT

KFUPM has piloted a novel high-severity fluid catalytic cracking (HS-FCC) process that can increase the yield of light olefins to 40wt% of the product, versus the normal 10wt%. The process combines mechanical modifications with changes in process variables and catalyst formulations. The main operating regime of this novel refining process is high reaction temperature, short contact time, high catalyst/oil ratio and a special down-flow reactor system. The paper presents a brief experimental study on the cracking of vacuum gas oil using equilibrated FCC catalyst in a 0.1 bbl/d circulating downer pilot plant. The results show a significant increase in the yield of light olefins, mainly propylene, as well as an improvement in gasoline quality and overall conversion. By adding 10wt% ZSM-5 to the catalyst, the pilot plant yielded 18wt% each of propylene and butylenes or a total increase of 37% compared to base catalyst. A comparative economics of a base refinery (with a conventional FCC) and an upgraded refinery (with HS-FCC) is presented. About 28% of return on investment can be achieved for propylene and para-xylene recovery in the upgraded HS-FCC refinery.

**Keywords:** Refining, Petrochemicals, Process Integration, FCC Light Olefins, Economics

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## 1. INTRODUCTION

The integration of refining and petrochemicals production is a major factor in lowering costs and improving efficiency. It also insures the security of feedstock supply to petrochemical producers. Integrated refining-petrochemical industry is continuously looking for processes with improved flexibility in producing various olefins from refinery products. Both industries are searching for opportunities by adding value to their products and product slates. Refiners are seriously looking for opportunities to improve their profits when refining margins are low. Providing more petrochemical feedstocks instead of fuels through innovative processes is gaining some earnest attention. Refiners and petrochemical producers have always benefited from their symbiotic relationship. However, this association is changing due to product-demand shifts by consumers. The petrochemical operator is continuously searching for lower cost feedstocks while the refiner is searching to add value to his products [Haelsig et al. 1997].

With the prevailing market, the value of FCC-derived petrochemical feedstocks is much higher than that of the FCC derived fuel products. Comparative economics showed that upgraded refinery with HS-FCC unit provides higher profitability than the corresponding stand-alone conventional refinery in the Gulf region. Therefore, to improve refining margins, it is about the right time to integrate refining with petrochemicals and get higher valued petrochemical feedstocks (propylene and aromatics) out of the refinery. In general, refining is driven by the gasoline market in North America and by diesel fuel in Europe, whereas in Asia, part of the refinery capacity is typically devoted to the production of petrochemical feedstocks, with fuels as a byproduct. Table 1 provides a list of typical sources of refinery-derived petrochemical feedstocks. Propylene and para-xylene are two key chemicals that can readily be produced from refinery streams.

The product slate from the fluid catalytic cracking (FCC) unit looks attractive when light olefins is desired. The FCC unit continues to be the dominant conversion process in the petroleum refinery, and increasingly its desired product slate is being shifted toward light olefins production. Despite the many technologies available to increase light olefins production in the FCC unit, an intense research activity in this field is still running, driven by its strong economic impact. The conversion of the FCC unit to maximal light olefins production requires hardware, process, and catalyst modifications. The conventional FCC process is being modified in a joint research project between KFUPM, Japan Cooperation Center, Petroleum (JCCP), and Saudi Aramco to a high-severity FCC process suitable for an integrated refinery-petrochemical complex [Fujiyama 1999] and [Maadhah et al. 2000]. The technology provides an olefin-driven process with the flexibility and performance capabilities to make it a key driver to refinery profitability.

Table 1. Sources of Refinery-Derived Petrochemical Feedstocks

| Petrochemical Feedstock | Refinery Stream | Refinery Process         |
|-------------------------|-----------------|--------------------------|
| Light Olefins           | VGO, Residues   | FCC, Visbreaking, Coking |
| BTX Aromatics           | Naphtha         | Catalytic Reforming      |
| LAB/Bio-detergents      | Kerosene        | Extraction of Paraffins  |
| Synthesis Gas           | Residues        | Gasification             |

## 2. PROCESS FEATURES OF HS-FCC

The process scheme of the HS-FCC process consists of several steps such as reaction, stripping regeneration, and separation. Oil feedstock is dispersed with steam and fed to the system, then contacted with the hot regenerated catalyst in a downer reactor and is catalytically cracked. Coke deposited on the catalyst is stripped with steam and transferred to the regenerator where air is introduced and coke on the catalyst is removed by combustion. The hot regenerated catalyst is returned to the reactor via a catalyst hopper at a controlled circulation rate to achieve heat balance of the system.

The main features of the HS-FCC process which comprise downer reactor, high reaction temperature, short contact time, and high catalyst/oil ratio are reviewed in the following paragraphs:

### 2.1. Down-Flow Reactor

A down-flow reactor system has been adopted for HS-FCC process. The catalyst and the feed flow downward along with gravity to minimize back mixing in the reactor and to obtaining a narrower distribution of residence time. The selection of an optimum residence time allows the maximization of intermediate products such as gasoline and light olefins. The down-flow reactor permits higher catalyst/oil ratio because the lifting of catalyst by vaporized feed is not required. As with most reactor designs involving competing reactions and secondary product degradation,

there is a concern over catalyst-feed contacting, back mixing, and control of the reaction time and temperature. The down-flow reaction would ensure plug flow without back mixing. Since the FCC process involves successive reactions, the desired products such as olefins and gasoline are considered intermediate products. A suppression of back mixing is the key to achieve maximum yield of these intermediates.

## **2.2. High-Reaction Temperature**

Conventional FCC is typically operated at low to moderate severity (510°C to 530°C riser outlet temperature) with flexibility to swing between maximum gasoline and maximum distillate mode. Attempts to operate the FCCU at high severity to produce more light olefins are not economically attractive because incremental light olefins will come at the expense of secondary cracking of gasoline. The secondary cracking of gasoline will result in excessive dry gas (C<sub>2</sub> and lighter) yields. While the FCCU has the capability of running at very high reactor temperatures, this approach is first being looked at to improve the conventional FCC process. The HS-FCC unit is operated under considerably higher reaction temperatures (550 to 650°C) than conventional FCC units. Under these reaction temperature, however, thermal cracking of hydrocarbons also takes place concurrently with catalytic cracking, resulting in increased undesirable products as dry gas and coke.

## **2.3. Short Contact Time**

The time-temperature relationship for the conventional FCC suggests there is an optimum operating window. If the residence time is too low, the bottoms cracking suffers while high reactor temperatures and long residence times promote dry gas production. The short residence time (less than 0.5 sec) of feed and product hydrocarbons in the downer should be favorable to minimize the thermal cracking. Furthermore, undesirable successive reactions such as hydrogen transfer reaction which consumes olefins produced primarily is depressed. In order to attain the short residence time, the catalyst and the products have to be separated immediately at the reactor outlet. For this purpose, a high efficiency product separator has been developed capable of suppressing side reactions (oligomerization and hydrogenation of light olefins) and coke formation accelerated by condensation.

## **2.4 High Catalyst/Oil Ratio**

In order to compensate the decrease in conversions due to the short contact time, the HS-FCC process have to be operated at high catalyst to oil ratios (C/O), in the range of 15 to 25. As mentioned earlier, the other advantage of operation at high C/O is the enhanced contribution of catalytic cracking against thermal cracking. Catalytic and thermal cracking proceed simultaneously in FCC reactions. It is well known that the ethylene yield is lower and isobutylene yield is higher in catalytic cracking compared to thermal cracking at the same conversion. By increasing the catalyst/oil ratio, the effects of operating at high reaction temperature (thermal cracking) are minimized. High C/O increases conversion and decreases temperature drop during the endothermic cracking reaction. Therefore, high C/O maintains heat balance and helps restrain thermal cracking, over-cracking, and hydrogen transfer reactions.

### 3. PILOT PLANT STUDY

#### 3.1. Experimental

Experiments were conducted in a downer-type pilot plant with a capacity of 0.1 bbl/d. The pilot plant consists of a downer reactor, stripper, regenerator, and catalyst hopper. Figure 1 presents a schematic flow diagram of the plant. Feed oil is charged into the upper part of the downer reactor together with dispersion steam. Regenerated catalyst is also charged to the top of the reactor from the catalyst hopper. At the outlet of the downer, product hydrocarbons are separated immediately from catalyst in the stripper, where heavy oil adsorbed on the spent catalyst is stripped by steam, and then spent catalyst is sent to the regenerator. Catalyst circulation rate is calculated from the delta coke and coke yield. Typical design parameters of the pilot plant test are presented in Table 2. All tests were conducted at 600°C and a catalyst/oil ratio of 40. The properties of the hydrotreated vacuum gas oil (VGO) of Arabian Light origin that was used as feed oil to the pilot plant are listed in Table 3. The base catalyst is a low cracking activity catalyst containing H-USY type zeolite with low acid site density supplied by CCIC, Japan. The catalyst was modified with 10wt% commercial ZSM-5 additive (supplied by Grace, USA). The ZSM-5 additive is widely used in the FCC process to increase octane at different silica/alumina ratios. The base catalyst and additive were deactivated with 100% steam at 810C for 6h before evaluation in a fluid-bed steamer.

Table 2. Typical Operating Conditions of the HS-FCC Pilot Plant

| Parameter                  |       | Value   |
|----------------------------|-------|---------|
| Reactor Outlet Temperature | °C    | 600     |
| Pressure (Stripper Top)    | kPa   | 98      |
| Inert Gas Rate             | mol/h |         |
| H <sub>2</sub> O           |       | 0.0-6.7 |
| N <sub>2</sub>             |       | 2.6     |
| VGO Feed                   |       |         |
| Rate                       | kg/h  | 0.4-1.2 |
| Preheat                    | °C    | 280     |
| Catalyst/Additive          |       |         |
| Inventory                  | L     | 6-10    |
| Steam Pretreatment @ 6h    | °C    | 810     |
| Rate                       | kg/h  | 13-45   |
| Cat/Oil ratio              | kg/kg | 13-45   |

Table 3. Properties of Hydrotreated Vacuum Gas Oil (VGO)

| Property                            | Value       |
|-------------------------------------|-------------|
| Density 15°C (g/cc)                 | 0.896       |
| Sulfur (wt%)                        | 0.19        |
| Nitrogen (ppm)                      | 440         |
| Conradson carbon (wt%)              | 0.07        |
| Pour point (°C)                     | 42.5        |
| Distillation data (°C): IBP/50%/FBP | 321/447/620 |

### 3.2. Results of Pilot Plant Tests

The base catalyst has a low-hydrogen transfer activity which is preferred for light olefins production. However, operating at high reaction temperature and high C/O ratio compensated for the low cracking activity of the base catalyst [Okuhara et al. (2001) and Aitani et al. (2000)]. Short contact time also suppressed hydrogen transfer reactions. Based on the intrinsic features of HS-FCC, maximum light olefins yield can be obtained by the combination of optimized catalyst system and operating conditions. In a reaction mechanism proposed by Buchanan (1991) for ZSM-5 addition and presented in Figure 2, the cracking of gasoline is accelerated because of the low the reactivity of paraffins compared to olefins.

The yields of light olefins, LPG, gasoline, LCO, HCO, and coke make are presented in Table 4 for conventional FCC and HS-FCC. In conventional FCC, the base catalyst yielded about 16wt% olefins and 43.4wt% gasoline compared to 29wt% light olefins and 45wt% gasoline in HS-FCC. In the case of ZSM-5 addition, the yield of light olefins increased to more than 37%, particularly propylene which showed an increase of 72%.

The results showed that ZSM-5 is highly selective toward propylene relative to Y-Faujasite containing base catalyst. In both cases, the rise in light olefins was accompanied with a drop in gasoline yield since the addition of ZSM-5 accelerates the cracking of gasoline to lighter products. The addition of ZSM-5 is effective in catalytic systems where the base catalyst have low-hydrogen transfer activity. The yield of light olefins for the base catalyst (with and without ZSM-5) increased with increasing conversion. However, increasing ZSM-5 content to 25wt% showed a minor increase in the yield of light olefins as presented in Figure 3.

Table 4. Comparison of ZSM-5 addition in Conventional FCC and HS-FCC

| Product Yields wt%         | Conventional FCC |                   | HS-FCC        |                   |
|----------------------------|------------------|-------------------|---------------|-------------------|
|                            | Base Catalyst    | Base +10wt% ZSM-5 | Base Catalyst | Base +10wt% ZSM-5 |
| Dry Gas                    | 5.3              | 6.4               | 4.6           | 5.5               |
| Propylene                  | 7.5              | 13.0              | 10.7          | 18.4              |
| Butylenes                  | 8.8              | 13.6              | 16.1          | 17.8              |
| <i>Total C3-C4 Olefins</i> | 16.3             | 26.6              | 28.7          | 39.3              |
| LPG                        | 20.7             | 29.3              | 30.9          | 40.5              |
| Gasoline                   | 43.4             | 34.1              | 45.4          | 34.0              |
| Light Cycle Oil (LCO)      | 15.0             | 15.4              | 9.4           | 9.3               |
| Heavy Cycle Oil (HCO)      | 14.3             | 13.4              | 6.6           | 7.1               |
| Coke                       | 2.3              | 2.1               | 3.1           | 3.5               |

#### 4. COMPARATIVE ECONOMIC EVALUATION

Typical product yields of conventional FCC and the two conceptual cases of HS-FCC modes used in the economic evaluation are presented in Table 5. Depending on the operating mode, the HS-FCC doubles the amount of light olefins and in another mode it provides three times more light olefins accompanied with a minimum loss in gasoline. The production of propylene is 2.1 to 3.6 times higher than the conventional FCC process. HS-FCC gasoline has a high octane number (RON about 100) and contains more heavy fractions. On the other hand, the content of olefins in the HS-FCC gasoline dropped by 50 to 85wt% depending on the operating severity.

A comparative economic evaluation has been conducted for a base refinery with conventional FCC unit and an upgraded refinery with an HS-FCC unit [Ino et al. (1998)]. The economics of the upgraded refinery has been evaluated using the relative internal rate of return (IRR) at prevailing prices of the second quarter of 1998. Both refineries were assumed at a location in the Arabian Gulf coast, with a capacity of 200,000 bbl/day each processing Arabian Light crude oil. The configuration of the base and upgraded refineries are presented in Table 6. The capacity of the conventional and HS-FCC units in both refineries was 36,000 bbl/day.

Table 5. Typical Yields of Conventional FCC and HS-FCC Used in Economic Evaluation

| Parameter                    | Conventional FCC | HS-FCC |        |
|------------------------------|------------------|--------|--------|
|                              |                  | Case 1 | Case 2 |
| Reaction temperature, °C     | 500              | 550    | 600    |
| Conversion, wt%              | 75               | 87     | 90     |
| Product Yield, wt%           |                  |        |        |
| Ethylene                     | 0.3              | 0.9    | 2.3    |
| Propylene                    | 4.2              | 9.3    | 15.9   |
| Butylene                     | 5.6              | 12.2   | 17.4   |
| Gasoline                     | 53.6             | 49.5   | 37.8   |
| Light Cycle Oil (LCO)        | 17.6             | 8.8    | 6.6    |
| Heavy Cycle Oil (HCO)        | 7.7              | 4.0    | 3.3    |
| Properties of Gasoline, vol% |                  |        |        |
| Olefins                      | 13.5             | 9.6    | 5.1    |
| Aromatics                    | 28.0             | 37.0   | 37.0   |

Table 6. Process Configuration of Base and Upgraded Refineries (1000 bbl/day)

| Process Unit                                   | Base Refinery | HS-FCC Upgraded Refinery |        |
|--|---------------|--------------------------|--------|
|  |               | Case-1                   | Case-2 |
| Crude Distillation                             | 200           | 200                      | 200    |
| Vacuum Distillation                            | 75            | 75                       | 75     |
| LPG Recovery                                   | 6             | 6                        | 6      |
| Naphtha HDS                                    | 49            | 49                       | 49     |
| Catalytic Reformer                             | 35            | 35                       | 35     |
| Benzene Extraction                             | 0.6           | 1.1                      | 2.1    |
| Kerosene Sweetening                            | 20            | 20                       | 20     |
| Gas Oil HDS                                    | 41            | 41                       | 41     |
| VGO Hydrotreater                               | 50            | 50                       | 50     |
| FCC/HS-FCC                                     | 36            | 36                       | 36     |
| MTBE   | 1.1           | 2.7                      | 3.9    |
| Alkylation                                     | 4.1           | 7.8                      | 10.9   |
| C4 Isomerization                               | 1.7           | 2.3                      | 4.2    |
| Visbreaker                                     | 31            | 31                       | 31     |
| Sulfur Recovery t/d                            | 238           | 238                      | 238    |
| H <sub>2</sub> Purification, m <sup>3</sup> /d | 1000          | 1000                     | 1000   |
| Propylene Recovery 1000 t/y                    | 0             | 148                      | 252    |
| Para-xylene Recovery 1000 t/y                  | 212           | 377                      | 601    |

#### 4.1 Results of Economic Evaluation

The economics of the upgraded refinery has been evaluated as an incremental economics from the base refinery. Incremental investment and IRR of propylene and para-xylene recovery are listed in Table 7. Incremental investment has been calculated from the difference in investment costs and the difference in returns between the two HS-FCC cases. The results showed that the HS-FCC case would give more profitability to the refinery. In both HS-FCC cases, the IRR reached 17 to 18%, while large investment is required to expand capacities of propylene, MTBE, and alkylation units. If para-xylene is to be recovered from the product slate, the IRR of the HS-FCC option reached 24 to 28% depending on the severity of operation, in spite of the larger investment needed to expand capacities of para-xylene, propylene, MTBE and alkylation units. Sensitivity analyses were performed to see the effect of 30% higher and lower prices of chemicals on the economics. It was found that higher para-xylene price enhances the profitability significantly. At 30% lower para-xylene price, the IRR obtained was 15%, while increasing its price 30% higher than the assumed average price; an IRR of 37% could be realized [Ino et al. (1998)].



Table 7. Incremental Investment and Internal Rate of Return (IRR)

| Parameter                          | Base Refinery | HS-FCC Upgraded Refinery |         |
|------------------------------------|---------------|--------------------------|---------|
|                                    |               | Case -1                  | Case -2 |
| <i>Propylene Recovery Option</i>   |               |                          |         |
| Incremental Investment MMS\$       | Base          | +106                     | +144    |
| Incremental Return, MMS\$          | Base          | +26                      | +37     |
| IRR, %                             | --            | 17.2                     | 17.9    |
| <i>Para-xylene Recovery Option</i> |               |                          |         |
| Incremental Investment MMS\$       | +200          | +332                     | +441    |
| Incremental Return, MMS\$          | +58           | +120                     | +186    |
| IRR, % (Para-xylene recovery)      | 20.1          | 24.3                     | 27.7    |

## 5. CONCLUDING REMARKS

Integrating refinery and petrochemical operations is an ongoing goal. With proper design and operation, the HS-FCC process is in best position to produce light olefins for petrochemicals usage. As per process technology, reactor configuration has a major impact on operating requirements, conversion and product selectivities. Catalytic cracking of VGO under high severity in a downer-type reactor boosts overall conversion and enhances the production of gasoline and light olefins. Moreover, it has been shown that the addition of ZSM-5 is effective in catalytic systems where the base catalyst have low hydrogen transfer activity. The results of economic evaluation showed that propylene and para-xylene production plays a major role in the economics of the upgraded refinery with HS-FCC option

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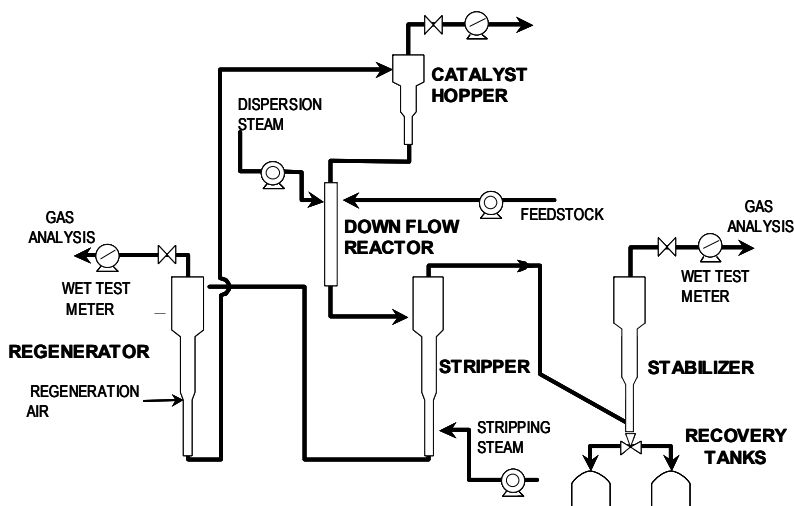


Figure 1 Flow diagram of pilot plant

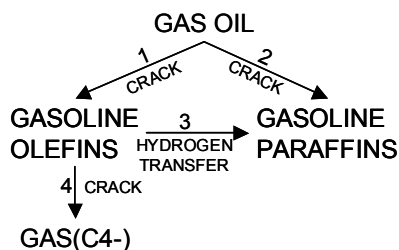


Figure 2. Simplified FCC Reaction Scheme [Buchanan (1991)].