

PRODUCTION OF LIGHT OLEFINS THROUGH GAS OIL CRACKING

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1. Introduction

Light olefins such as ethylene, propylene, and butylenes, are basic building blocks for petrochemicals. Further, these olefins are also useful for production of clean fuels such as alkylates – which have high octanes but no sulfur, olefins, and aromatics – or as octane-enhancers such as ethers. The conventional olefin production process is steam cracking of C₂–C₄ light paraffins from natural gas or from refinery gas streams. However, the increasing demand for gaseous fuel and the rising price of natural gas have limited the supply of light hydrocarbons.

Fluid catalytic cracking (FCC) is traditionally the dominant refinery conversion process for producing high-octane gasoline. Driven by an increased demand for light olefins worldwide, FCC is also an option to yield petrochemical feedstocks from heavy oils through the innovation of hardware, operating parameters, and catalyst formulation.¹ In this respect, a number of FCC-derived technologies have been developed,² including:

- Deep Catalytic Cracking (DCC) and the Catalytic Pyrolysis Process (CPP) by the Research Institute of Petroleum Processing, SINOPEC;^{3,4}
- Ultimate Catalytic Cracking (UCC) by Indian Oil;⁵
- High Severity (HS) FCC jointly developed by the Petroleum Energy Centre (Tokyo) and the King Fahd University of Petroleum and Minerals.^{6,7}

Some catalyst companies, including Albemarle, are producing or in the process of designing catalysts or additives for this technology. The technology advancement in this area is useful since the demand for heavy product fractions tends to decrease steadily. It has been demonstrated that in the production of light olefins from heavy oils, several factors including feed quality, catalyst type, reactor temperature, and catalyst/oil ratio strongly influence the yields.

This paper deals with a hydrocracker bottoms vacuum gas oil (HCB VGO) from a Canadian bitumen-derived heavy oil. For comparison, selected data from cracking an aromatics-rich VGO will also be presented orally at the conference but not in this manuscript.

2. Experimental

Feed HCB VGO was cracked in a fluid-bed microactivity test (MAT) unit at 515–670°C in the presence of a specialty catalyst AFX-2A from Albemarle's AFX (Advanced Fuels eXperimental) series, in conjunction with a conventional FCC catalyst, Centurion HA (CENT-HA), also from Albemarle. Details of the experiments were reported elsewhere.⁸ Tables 1 and 2 show the properties of the feed and catalysts in this study.

Table 1. Feed Properties

Feed	HCB
Density @ 15 °C, g/mL	0.8643
Total sulfur, wt%	<0.001
Total nitrogen, wppm	<0.0001
343 °C-, wt%	19.6
524 °C+, wt%	1.4
Aromatics, wt%	9.3
Gasoline precursors,^a wt%	97.0

^a Saturates + monoaromatics

Table 2. Properties of Laboratory-Deactivated Catalysts

Catalyst	AFX-2A	Centurion-HA
Surface area, m²/g		
Total	185	154
Matrix	87.3	71.1
Zeolite	98.2	82.3
Al₂O₃, wt%	46.3	56.2
SiO₂, wt%	49.5	39.1
Re₂O₃, wt%	Proprietary	2.64

To differentiate thermal cracking from catalytic cracking, HCB VGO was also cracked with sand under the same conditions. After cracking, the gasoline fraction was characterized with a PIONA analyzer for hydrocarbon type. Conversions and yields of gaseous olefins, coke, gasoline, and components in the gasoline fraction (e.g., total saturated or unsaturated naphthenes, iso-paraffins, n-paraffins, and aromatics with a breakdown of benzene, toluene, and xylenes+ethyl benzene) from different reaction systems were compared.

3. Results and Discussion

3.1. Catalyst versus Sand

Catalysts enabled both catalytic reactions and thermal cracking while sand enabled only thermal cracking. In general, both solid-systems could produce high yields of light olefins at certain conditions. However, the cracking characteristics and product distributions were different. Figure 1 shows that catalytic cracking prevailed at low temperatures whereas pyrolysis was favored at high temperatures. Pyrolysis exhibited non-selective cracking with similar amounts of C₂ to C₄ olefins produced, while catalytic cracking favored the production of C₃ and C₄ olefins over ethylene. At high temperatures, a reactor with sand could produce more ethylene than its counterpart with catalysts. This was due to differences in reaction mechanisms involving carbocation intermediates in catalytic cracking and free radicals in thermal cracking.

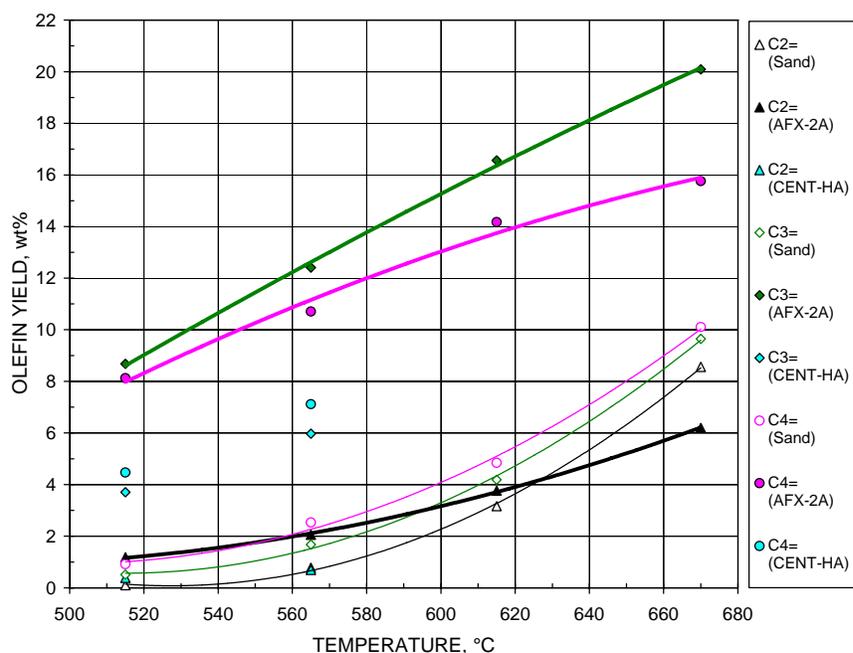


Figure 1. Variation of C₂ to C₄ Olefin Yields with Temperature at 6 C/O Ratio

Figure 2 shows that as temperature increased, conversions and yields of gasoline and coke from the two solid-systems increased, with the exception of gasoline yield from catalytic cracking. At high temperatures, pyrolysis produced much more diolefins but very little coke compared with catalytic cracking.

3.2. Effect of catalyst type

The specialty catalyst contained a significant amount of restricted-pore molecular sieves, which were particularly selective to light olefins production but not efficient in cracking large molecules. In comparison, the conventional FCC catalyst contained more active ingredients with mesopores for precracking the high-boiling fractions in the feed. Thus, at fixed conditions, the specialty catalyst produced more light olefins through overcracking of gasoline than the conventional FCC catalyst, which produced more gasoline and coke. At elevated temperatures, both catalysts gave higher conversions (Figure 2) and yields of olefins (Figure 1) but lower yields of gasoline (Figure 2). The specialty catalyst produced olefins in the order propylene > butylenes > ethylene while the conventional FCC catalysts produced olefins in the order butylenes > propylene > ethylene. This suggests that some C₄ olefins could be cracked by active ingredients in the specialty catalyst. The coke yields from both catalyst-systems were more sensitive to the catalyst/oil ratio than to the temperature. The higher the severity, the more coke produced.

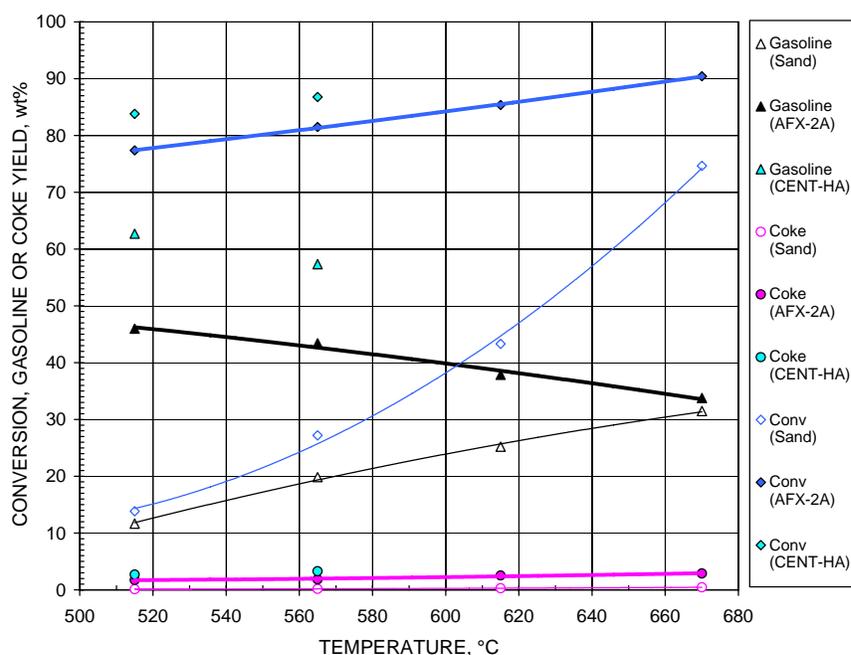


Figure 2. Temperature Effect on Conversion, Gasoline, and Coke Yields at 6 C/O Ratio

3.3. Effect of Feed

Although not shown in this paper, results in a separate study demonstrate that, at the same conditions, the aromatics-lean feed gave higher conversion and olefins yield than its counterpart with more aromatics. This can be explained because refractory aromatic rings are not crackable without hydrogen at high pressure, although the side chains of aromatics can be detached and fragmented.

3.4. Liquid Product Characterization

Figures 3a and 3b depict PIONA analysis of the gasoline fraction of the MAT liquid product. They indicate the following.

- Aromatics, being uncrackable, increased at the expense of paraffins and naphthenes at higher temperature. Aromatics were always the most, or one of the most, abundant species.
- In cracking with the specialty catalyst, the next major product was s-naphthenes, followed by s-i-paraffins (the two yields were in the same order), us-naphthenes, us-n-paraffins, s-n-paraffins, and us-i-paraffins (note: “saturated”, “unsaturated”, “normal” and “iso” were abbreviated by prefixes “s-”, “us-”, “n-”, and “i-”, respectively).
- However, when the conventional FCC catalyst was used, s-i-paraffins were much higher than s-naphthenes, which was followed by us-i-paraffins, us-n-paraffins, s-n-paraffins, and us-naphthenes. In this case, the yield of aromatics was just slightly lower than that of s-i-paraffins.

The enrichment of aromatics in the gasoline fraction contributed to higher octane numbers and specific gravity, which could be correlated with aromatics contents independent of the catalyst type and inert sand. Among the aromatic components, the yields increased with the carbon number. This was expected as the number of isomers increased at a higher carbon number. However, the yield of C₁₀ aromatics dropped significantly, as the gasoline cut point was set at 200°C in PIONA analysis.

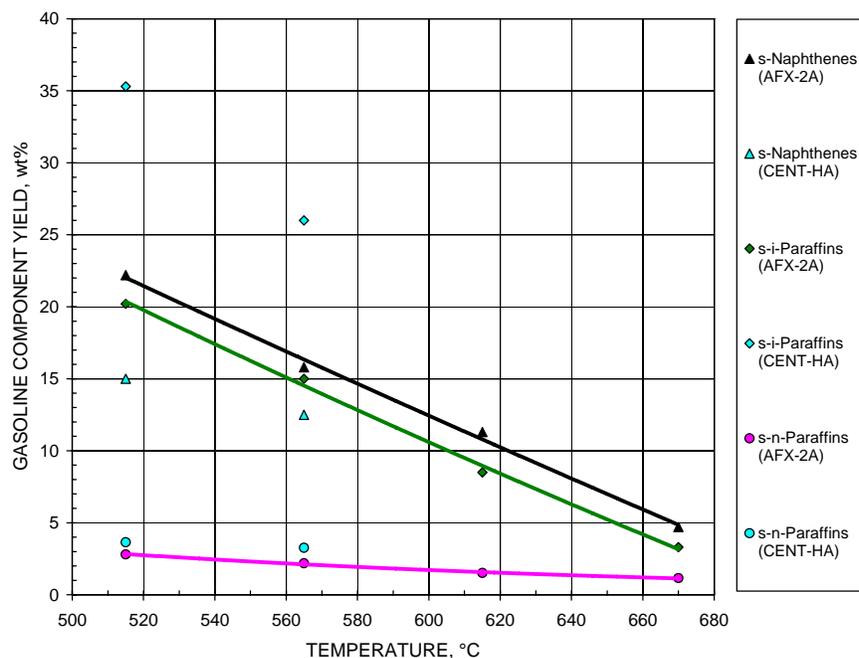


Figure 3a. Gasoline Composition 1 versus Reactor Temperature at 6 C/O Ratio

4. Conclusions

Production of light olefins through catalytic cracking of gas oil is a viable technology which offers some advantages over steam cracking: (1) lower reaction temperature; (2) lower capital and production costs with existing FCC facilities; (3) higher flexibility in adjusting the product slates between light olefins and high-octane gasoline. There are several commercial units with this high-olefins FCC technology in China and Thailand. In Alberta, Canada, the option is being considered to cope with the future overproduction of bitumens from oil sands, as well as to support the local petrochemical industry.

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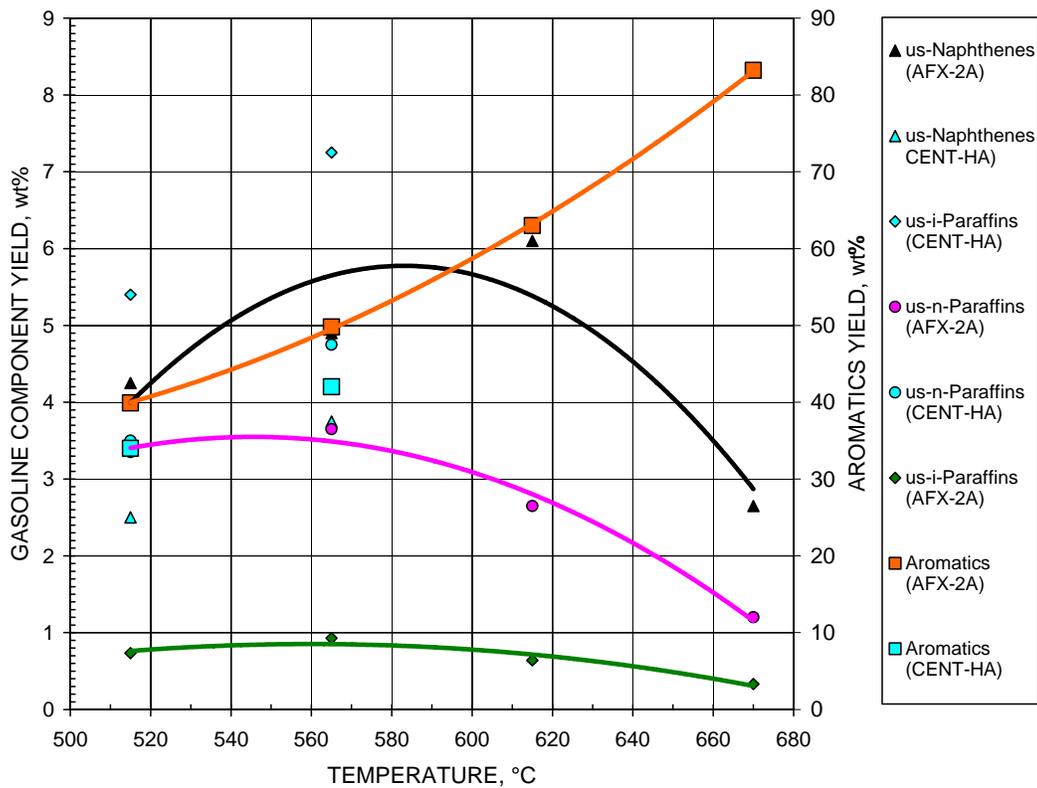


Figure 3b. Gasoline Composition 2 versus Reactor Temperature at 6 C/O Ratio

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