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# Production of Liquid Biofuels in a Fluid Catalytic Cracking Pilot-Plant Unit Using Waxes Produced from a Biomass-to-Liquid (BTL) Process

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The production of synthetic transportation fuels from lignocellulosic biomass feedstocks through a biomass-to-liquid (BTL) process based on Fischer–Tropsch (F–T) synthesis is today of increasingly importance. Depending on the operating conditions of the F–T process, heavy waxy hydrocarbons could be produced (waxes) with almost zero aromatics and sulfur. The purpose of this study is the investigation of a catalytic cracking process for the upgrading of these BTL waxes in order to produce high-quality biofuels. In this work, a F–T Wax with hydrocarbons up to C<sub>40</sub> was used, while the fluid catalytic cracking (FCC) experiments were carried out in an FCC pilot-plant unit operating in a full circulation mode with continuous catalyst regeneration. Three different catalysts, cofeeding options, and various operating conditions were investigated in the pilot plant. Our results showed that the F–T Wax is very crackable and conversions in the range of 70–90 wt % (on the feed) can be achieved with all catalysts tested. Catalyst type and cracking temperature also play an important role in improving the selectivity of specific FCC products. The process gives high gasoline yields with very low aromatics, low light cycle oil yields, and very low coke yields. The use of a ZSM-5 catalyst offers also significant advantages for the production of light olefins, while this catalyst strongly influences the gasoline composition.

## 1. Introduction

The declining petroleum sources, the increased demand for transportation fuels, and the environmental concerns about conventional (petroleum) fuels necessitate research for the production and use of new sources of fuel. There is today a steady trend in refineries toward using higher density, higher sulfur, and more acidic crudes. In the future, a significant growth is expected in using oil-sands and other nonconventional sources. At the same time, there is a strong requirement for the production of cleaner fuels. Thus, there are today a lot of challenges to the petroleum industry that require new investments to meet forecast demand growth and maintain profitability. The key issue of the refining industry is to produce fuels with a better composition compared with conventional fuels, i.e., with less sulfur, nitrogen, aromatics, and olefins and more naphthenes and isoparaffins.<sup>1</sup>

Biofuels, besides other benefits (to domestic agriculture, security of supply, etc.), produce less greenhouse gas emissions than fossil fuels and could be a solution for better quality fuels. The EU vision for 2030 is that biofuels should cover about 20% of the fuel market. The first-generation biofuels have already been introduced in the fuel market in many places. However, the high cost of these fuels and the Life Cycle Analysis (LCA) concentration dictates that these biofuels should be replaced by second-generation biofuels that are based on lignocellulosic biomass.<sup>2</sup> One very good option for biofuels production is to use biomass-derived feeds in a conventional petroleum refinery. Through use of the existing refinery infrastructure, biofuels could be produced in a cost-effective way.<sup>3</sup>

Among other technologies for the production of a second-generation biofuel is the production of transportation fuels from lignocellulosic biomass through a route that is similar with the existing gas (or coal)-to-liquid (GTL or CTL) technology.<sup>4,5</sup> This route includes initially a biomass gasification step in order

to produce synthesis gas (CO + H<sub>2</sub>). The hot gas from the gasifier requires the removal of sulfur compounds and tar. A water–gas shift reactor is sometimes necessary to achieve a H<sub>2</sub>/CO molar ratio of 2. This mixture is introduced into the Fischer–Tropsch (F–T) reactor for the production of synthetic fuels, which consist mainly of heavy hydrocarbons with almost zero aromatics and sulfur compounds. The boiling range of the hydrocarbons produced from F–T synthesis depends on the conditions and on the catalyst of the F–T reactor. A low-temperature F–T synthesis produces a very high amount of waxy hydrocarbons with high boiling and melting points. In the existing commercial GTL or CTL technologies, this F–T Wax is subsequently converted to diesel and other lighter fuels usually via hydrocracking. Although GTL and CTL are established technologies, the above-mentioned biomass-to-liquid (BTL) process is a completely new approach that requires the development of new technologies (biomass treatment, biomass gasification, hot gas cleanup, new F–T catalysts, and advanced Wax upgrading) especially toward a reduction of the cost of the process.<sup>6–9</sup> The big advantage of these BTL fuels (which makes them a very attractive option to the automotive industry) is that they are directly usable in the present day in transportation sector and furthermore they may be suitable for future fuel cell vehicles via on board reforming since they are free of sulfur.

As was mentioned above, the hydrocracking of F–T Waxes is an established technology that is very attractive for diesel production but not for gasoline.<sup>10,11</sup> Hydrocracking technology requires high pressures and hydrogen consumption, and it produces less valuable saturated gases. On the contrary, previous studies in the literature showed that Wax feedstocks (from various sources) could be an attractive feed for the fluid catalytic cracking (FCC) unit.<sup>13–17</sup> Moreover, the fuels that would be used in future car engines (HCCI) would be more of a naphtha type with high paraffinic and low aromatic content. For production of these new fuels, Wax catalytic cracking may play an important role.

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**Table 1. Properties of the FCC Feeds Used in This Study**

	API	SG	S, ppm	N, ppm	CCR, wt %	ASTM D2887 (wt %/°C)				
						5	30	50	70	95
Wax	43.1	0.8104	<3	<3	0.006	368	396	413	432	474
VGO	26.1	0.8977	2300	622	0.02	266	357	401	441	528

**Table 2. Catalyst Properties**

	Ecat	steamed FCC catalyst
TSA (m <sup>2</sup> /g)	178	157
ZSA (m <sup>2</sup> /g)	58	40
UCS (Å)	24.26	24.26

Other options for upgrading the F–T Wax were also considered in the literature like steam (thermal) cracking.<sup>12</sup> However, the FCC process is the most widely used process for the conversion of heavy fractions of crude oil into more valuable products [gasoline, diesel, and liquefied petroleum gas (LPG)]. This process offers a lot of flexibility to refiners and, thus, F–T Waxes could be used at least as cofeeds in the FCC unit. In the past, many studies have been presented in the literature using different bioliquids as cofeeds in the FCC process.<sup>3,18</sup>

The objective of the work presented in this paper is the upgrading of a F–T Wax via an FCC process. The cracking tests were carried out in a fully circulating fluid-bed FCC pilot-plant unit. The performance of Wax cracking was investigated as a function of different operating variables like the cracking temperature, catalyst to oil ratio, cofeeding, and type of catalyst. Special emphasis was given on the quality of the produced products based on detailed hydrocarbon analysis.

## 2. Experimental Section

**2.1. Feedstocks.** A commercially available F–T Wax feed and, for comparison, a conventional hydrotreated vacuum gas oil (VGO) were used in this work. Blends of the two feeds were also used in order to investigate coprocessing options. Both feeds were characterized in CPERI using standard ASTM methods, and some of their characteristic properties are given in Table 1. The gas chromatography/mass spectrometry (GC/MS) analysis of the Wax (not shown in the figure) showed that this feed is highly paraffinic with hydrocarbons up to about C<sub>40</sub>. The melting point of the Wax was 80 °C.

**2.2. Catalysts.** Three catalysts were used in this study for the catalytic upgrading of the F–T Wax. Two of them were selected from a catalyst prescreening study performed in CPERI using a short-contact-time MAT (SCT-MAT) unit.<sup>17</sup> These two catalysts were an FCC catalyst suitable for highly hydrotreated feeds (named in this paper as FCC) and a conventional ZSM-5 additive (named in this paper as ZSM-5). Albemarle supplied both of these catalysts. The FCC catalyst contained a medium concentration of a proprietary novel zeolite. The conventional ZSM-5 additive was a commercially available ZSM-5 additive (ZOOM) with a high percentage of ZSM-5 crystals. Blends of the FCC catalyst with ZSM-5 in different concentrations were tested as well. Both FCC and ZSM-5 catalysts (and their blends as well) were tested in the pilot plant after a steaming deactivation procedure in a fluid-bed reactor at 788 °C for 12 h using 100% steam. Some selective properties of the steamed FCC catalyst are given in Table 2. For comparison purposes, a low-activity conventional equilibrium catalyst (named in this paper as Ecat) with low rare-earth and low metals (Ni and V) was also tested in this work. The properties of the two FCC catalysts are given in Table 2.

**2.3. Experimental Unit.** All experiments of this study were carried out in CPERI FCC pilot-plant unit.<sup>19</sup> This unit has been

extensively used for FCC studies in cooperation with many petroleum companies worldwide. From these studies, it was proved that it presents an excellent simulation of the commercial FCC unit performance. The pilot plant (Figure 1) operates in a full catalyst circulation mode with continuous regeneration and consists of a riser reactor (7 mm i.d. and about 9 m height), a stripper, a lift line, and a fluid bed as the regenerator (78 mm i.d.). The catalyst circulation is achieved with two slide valves, and it is controlled in a manner similar to that in a commercial FCC unit. There is independent temperature control over many zones in the reactor, which can permit, for the entire system, an isothermal operation mode. For catalyst stripping, steam is used at the bottom of the stripper vessel. The separation of the produced gaseous and liquid products takes place using a specially designed refrigerated stabilizer. The liquid products, mainly C<sub>5</sub> and heavier, are condensed and collected. The pilot plant is fully automated, and its process control system is based on a special industrial control system.

In each FCC pilot-plant test, the coke, flue, and cracked gases and the total liquid product yields are measured. From the total liquid product, the yields of gasoline, light cycle oil (LCO), and heavy cycle oil (HCO) are determined using a GC simulation distillation method (ASTM D2887). The produced cracked gases, the flue gases, and the liquid products are measured with accuracy using a system of gas chromatographs, wet test meters, and weight balances. The gasoline hydrocarbon composition was measured by PIONA analysis (ASTM D5134) using a GC/DHA analyzer. The gasoline RON/MON was estimated based on the PIONA analysis using theoretical models (GC RON/MON).

## 3. Results and Discussion

**3.1. Coprocessing of Wax and VGO.** In order to investigate the performance of the Wax feed under catalytic cracking experiments and to compare this performance with a conventional hydrotreated VGO, a study was initially performed in the pilot plant using the two feeds. However, because Wax produced from biomass will probably not be available in large volumes, at least not for some years, a VGO/Wax coprocessing option was also investigated in the present study using two Wax/VGO blends with 20/80 and 50/50 (w/w) portions. For all of these tests, a typical refinery Ecat (described in section 2.2) was used, while the experimental conditions in the FCC pilot plant are listed in Table 3. The main parameter in these experiments was the C/O ratio, which was adjusted using different preheat temperatures. In this way, experiments at a range of different conversions were performed.

Figure 2 presents the crackability (conversion vs C/O) of the two feeds and the two blends and shows that the Wax is much more crackable than the hydrotreated VGO. As we mix more Wax in the VGO, the blend becomes more crackable. This is due to the highly paraffinic nature of the Wax molecules compared with VGO, which contains some aromatic compounds.<sup>14,15</sup> Even with a minimum amount of catalyst (C/O = 3) the Wax is very crackable, achieving conversions of around 63 wt %. The necessary C/O ratios to achieve the same conversion level (75 wt %) from all four feeds are given in Table 4. The coprocessing option seems to be beneficial for a refinery because, by introduction of even 20 wt % Wax in the VGO,

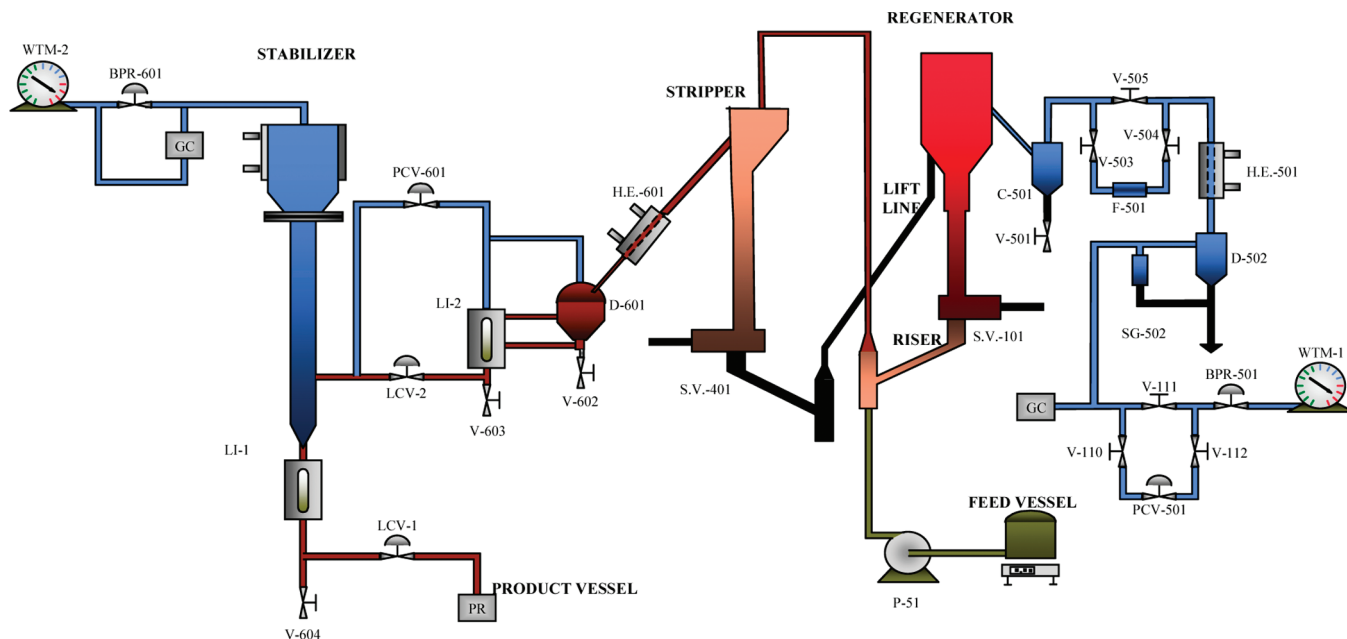


Figure 1. Schematic diagram of CPERI FCC pilot-plant unit.

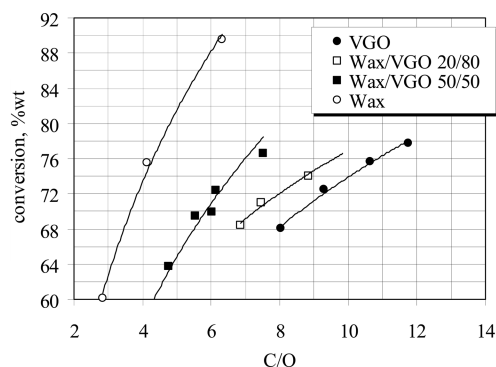


Figure 2. Crackability comparison of Wax, VGO, and Wax/VGO blends (catalyst, Ecat;  $T = 538\text{ }^{\circ}\text{C}$ ).

Table 3. FCC Pilot-Plant Operating Conditions

isothermal riser temperature ( $^{\circ}\text{C}$ )	538
regenerator temperature ( $^{\circ}\text{C}$ )	710
hydrocarbons partial pressure (psia)	14
feed rate (g/min)	25

Table 4. Product Yields (wt % on the Feed) at 75 wt % Conversion

	C/O	gasoline	coke	dry	LPG	LCO	RON	MON
VGO	10.7	52.0	2.95	1.70	18.3	18.6	95.2	83.1
Wax/VGO (20/80)	9.3	51.8	2.47	1.55	18.9	16.7	94.4	82.3
Wax/VGO (50/50)	6.9	50.1	1.82	1.49	21.6	12.4	93.4	81.2
Wax	4.4	48.5	0.6	1.23	24.8	3.8	90.9	79.1

the conversion could be increased by about 4 wt % compared to VGO operation.

In Figure 3, we present the coke yield versus conversion for the four feedstocks. This figure shows that the Wax produces much lower coke compared with VGO, while the blends give coke yields between the two feeds. The coke yield from the VGO increases rapidly above 70 wt % conversion and reaches values up to about 3.0 wt % (on feed) at 75 wt % conversion. This is due to the fact that at higher conversions the remaining VGO molecules (that are available for cracking) are mainly refractory aromatic molecules. These molecules are responsible for coke production due to polymerization and condensation reactions (coke precursors). On the contrary, the curve of coke yield versus conversion for the Wax feed (Figure 3) is almost

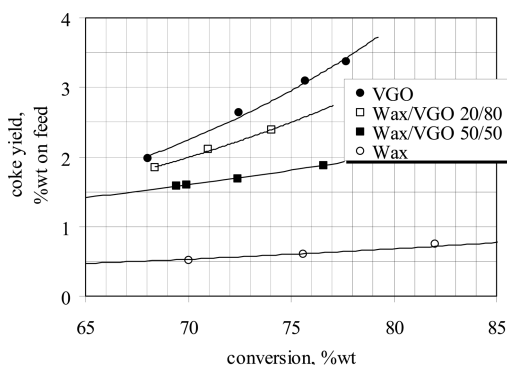


Figure 3. Coke yield vs conversion (catalyst, Ecat;  $T = 538\text{ }^{\circ}\text{C}$ ).

linear up to very high conversion levels of 95 wt %. The slope of this curve is relatively low, and the coke yields, produced from this feed, are between 0.4 and 0.8 wt %. This is due to the absence of aromatic compounds or coke precursors even at very high conversion. The coke produced from Wax cracking originates mainly from secondary polymerization reactions of the (rich) olefinic fraction or from some hydrogen-transfer reactions.<sup>14,15</sup> The slopes of the curves for the two blends are between those of Wax and VGO. The coke yield is very important for the heat balance of the FCC unit. The coke made by the catalytic cracking of Wax is probably too low to give sufficient energy to the FCC unit. Using the coprocessing option with (for example) 20 wt % Wax in VGO, we could decrease by about 15% the coke yield (in comparison to VGO) without problems in the heat balance of the unit. Moreover, this coprocessing option is also important for a refinery working in resid operation for better control in the regenerator temperature and for the introduction of more resid in the feed.

In Figure 4, we present the gasoline yields for the four feedstocks. The figure shows that the yield of gasoline ( $\text{C}_5\text{--}221\text{ }^{\circ}\text{C}$ ) produced from the F–T Wax is less than that from VGO and less than those from the two blends at least up to about 80 wt % conversion. At this conversion, there is overcracking in the gasoline from VGO and in the gasoline from the 50/50 blend. On the contrary, there is no overcracking in the gasoline from Wax and in the gasoline from the 20/80 blend. Even at 90 wt

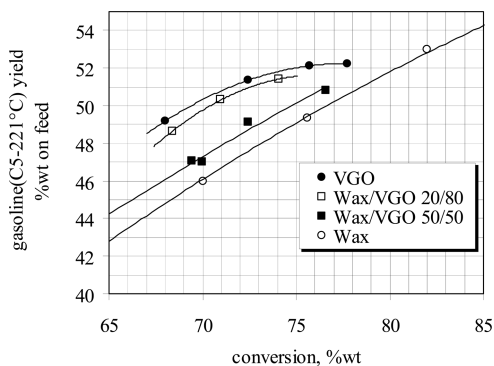


Figure 4. Gasoline yield vs conversion (catalyst, Ecat;  $T = 538\text{ }^{\circ}\text{C}$ ).

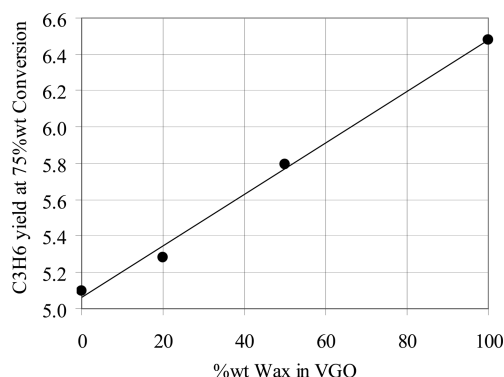


Figure 5. Propene yield from the coprocessing of Wax and VGO (catalyst, Ecat;  $T = 538\text{ }^{\circ}\text{C}$ ).

% conversion, we have not observed any overcracking in the gasoline from Wax. This shows that the gasoline components are relatively stable and that they do not crack easily to lighter components. This conclusion will also be confirmed later when we discuss the temperature effects on Wax cracking.

In Table 4, we summarize the comparison between the four feedstocks regarding the yields of some main FCC products at 75 wt % conversion. Table 4 shows that the LCO yield (221–343  $^{\circ}\text{C}$ ) is much less from the Wax cracking compared with that from VGO. As we mix more Wax into the VGO, less LCO is also produced. This is due to the high crackability of the LCO molecules that are produced from the Wax. These molecules are highly paraffinic with long chains and, consequently, they easily crack to lighter molecules within the gasoline and LPG boiling range.

As we discussed above, the yield of gasoline ( $\text{C}_5\text{--}221\text{ }^{\circ}\text{C}$ ) produced from the F–T Wax (at 75 wt % conversion) is less than that from the VGO (up to about 80 wt % conversion), while the LPG yield is much higher (Table 4). This is due to the more crackable nature of the Wax that undergoes cracking reactions, producing more LPG gases as primary products (as  $\text{C}_3$ 's and, especially, as  $\text{C}_4$ 's). From the LPG gases, the LPG olefins are more favored. In Figures 5 and 6, we present the propylene yield and the  $\text{C}_4$  olefinicity ( $\text{C}_4=\text{total C}_4$ ) (at 75 % conversion) as a function of the level of Wax cofeeding. It is clear that the propylene selectivity and  $\text{C}_4$  olefinicity increase with an increase of the Wax concentration in the VGO. Wax cracking could give 1.5 wt % more propylene than VGO cracking. This is another benefit for the refinery from a Wax/VGO cofeeding option. By the addition of Wax in the feed, the refinery could increase LPG olefins. Higher yields of these components could have a considerable effect on the profitability of the refinery. The results of Figures 5 and 6 show that there is a linear correlation between the selectivity of these products

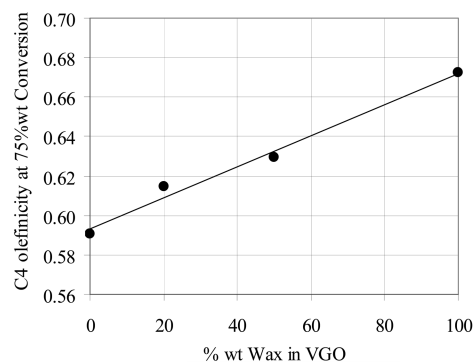


Figure 6.  $\text{C}_4$  olefinicity from the coprocessing of Wax and VGO (catalyst, Ecat;  $T = 538\text{ }^{\circ}\text{C}$ ).

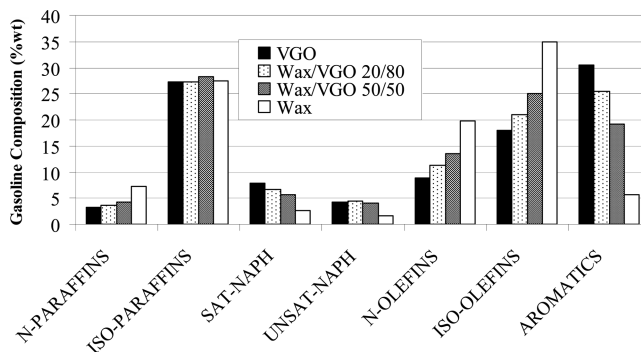


Figure 7. Gasoline composition at 80 wt % conversion from the coprocessing of Wax and VGO (catalyst, Ecat;  $T = 538\text{ }^{\circ}\text{C}$ ).

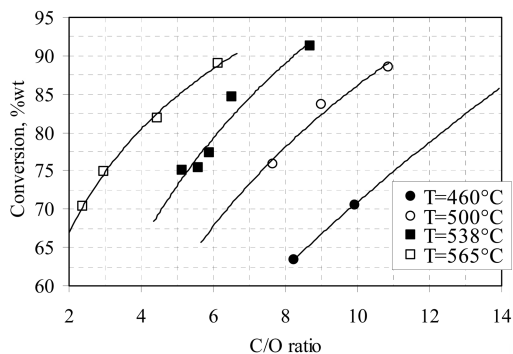
and the Wax content in the VGO. This is also valid for the selectivities of the other products. This concludes that there are no significant synergetic effects between the Wax and the (hydrotreated) VGO and, thus, the adsorption constants of the two feeds are similar.

Table 4 also shows that the quality of the gasoline produced from VGO cracking is better than that from Wax cracking (regarding RON and MON). Both octane numbers in the Wax gasoline are about 3–4 units lower than those in the VGO gasoline. Of course, the two blends have octane numbers between the VGO and Wax operation. Our pilot-plant results (not presented in the figures) show that the RON of the Wax gasoline is almost constant and only slightly dependent on the conversion because of the low aromaticity of this gasoline<sup>10</sup> even at very high conversions. The RON of the gasoline produced from the VGO increases substantially with conversion because of the enrichment of this gasoline in aromatic compounds.

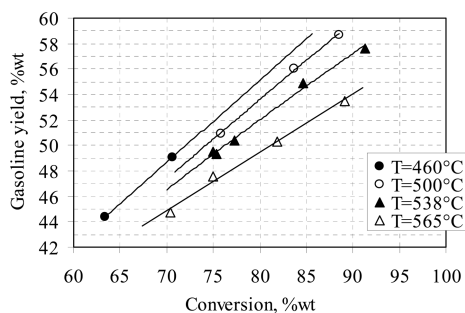
The explanation for that above comes from the compositions of the four gasolines that are depicted in Figure 7 (from PIONA analysis). The gasoline from the Wax contains a very low aromatic content compared with the VGO gasoline. Moreover, by cofeeding the Wax into the VGO, we could also decrease the aromatic content at least 20%. This is of special importance for new gasoline specifications regarding low aromatic content. It must be noted that the corresponding aromatic content of gasoline produced using a conventional VGO is more than 30 wt % (Figure 7). The Wax gasoline contains much higher olefins [both normal (N) and ISO] than the VGO gasoline. The N-paraffins are also higher in the Wax gasoline, while the ISO-paraffins are slightly higher in the VGO gasoline.

The results of the present study are comparable to others in the literature.<sup>14,17</sup> Despite the fact that different experimental units were used (a microriser in ref 14 and a fixed bed in ref 17), it seems that the general trends (regarding the effect of the





**Figure 8.** Effect of the C/O ratio and cracking temperature on Wax conversion (catalyst, FCC).

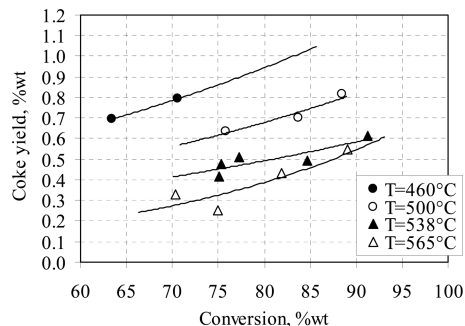


**Figure 9.** Effect of the cracking temperature on the gasoline yield (catalyst, FCC).

temperature or/and conversion) are consistent in all units. Consequently, scale-up effects in Wax catalytic cracking seem to be not significant. Of course, there are differences between the various studies regarding product selectivities; however, these differences could be justified by the differences in the Wax feed quality or base catalyst used. For example, in ref 14, the conversion achieved with a heavy Wax at C/O = 4 and residence time = 2 is about 85 wt %, while that in the present study is around 75 wt %. The LCO selectivity in ref 14 is higher compared with that of the present study. However, as was mentioned above, both Wax feeds and product cut points are different in the two studies and, thus, it is difficult to have side-by-side comparisons of the two units.

**3.2. Effect of the Cracking Temperature on Wax Cracking.** In order to investigate the effects of the cracking temperature on Wax conversion, a study was performed in the FCC pilot plant using the low-activity FCC catalyst and the Wax feed. Figure 8 shows that the temperature has a strong influence on conversion. Even at the lowest temperature (460 °C), we can achieve high conversion levels up to 70 wt % at C/O = 10.

Regarding the gasoline yield (Figure 9), as anticipated, it is optimized at higher conversions and lower temperatures. With this catalyst, gasoline overcracking was not observed even at 90 wt % conversion. The maximum gasoline yield achieved with the Wax feed at 80 wt % conversion was about 55 wt % (on feed) at the lowest temperature but based on extrapolation. At 500 °C, the maximum (interpolated) gasoline yield achieved with the Wax feed at 80 wt % conversion was about 54 wt % (on the feed). Figure 9 shows that even at very high conversions (high C/O ratios) or at very high temperatures gasoline overcracking is not observed. This shows that the gasoline components are relatively stable and that they do not crack easily to lighter components. From the detailed hydrocarbon analysis (not presented in the figures), it appears that from the gasoline



**Figure 10.** Effect of the cracking temperature on the coke yield (catalyst, FCC).

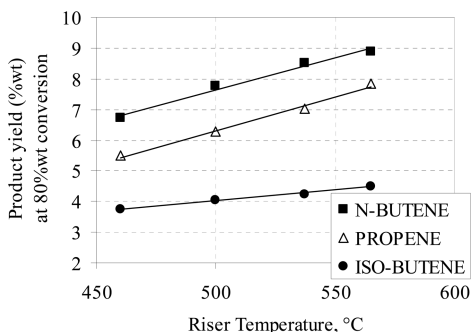
hydrocarbons only the N-olefins and at the highest temperature of 565 °C tend to overcrack at conversions higher than 80 wt %.<sup>20</sup>

As is shown in Table 4, the diesel (LCO) yield was very low from Wax cracking with Ecat. This was validated from the tests with the FCC catalyst where the LCO yield (not given in the figure) was always below 4 wt % (on the feed). Moreover, the LCO yield was only slightly affected by conversion and by temperature. It was higher at lower conversions and lower temperatures. As was also discussed in section 3.1, this low LCO yield is expected because the LCO is an intermediate cracking product. It appears that at high temperatures the LCO molecules crack further to smaller compounds (gasoline and gases) because of their high paraffinic nature. Our first measurements with a GC/MS technique (not presented in the figure) validate that this LCO is highly paraffinic and, thus, of a better quality than the conventional LCO from the VGO. We expect also a satisfactory degree of branching in LCO hydrocarbons, which is important for its cold-flow properties. Of course, this degree of branching should be lower than that of gasoline because the ratio of the rate of cracking over the rate of isomerization is expected to increase with the length of the chain of the hydrocarbons.<sup>14–16</sup>

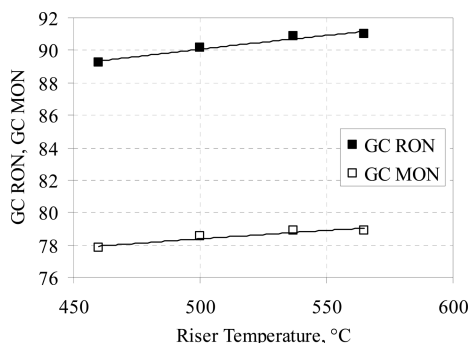
Coke is a very important product for the process heat balance. As with Ecat (Figure 3), the coke yield at high temperatures is very low and it is slightly affected by the conversion level (Figure 10). In agreement with the cracking results from a conventional VGO, the coke yield from the Wax is maximized at high conversions and low temperatures. The coke yield observed at the lower temperature of 460 °C is higher compared with that from 560 °C. The difference in the coke yields shown in Figure 10 is mainly an effect of the C/O ratio. To achieve the same conversion at these two different temperatures, higher C/O ratios are required for the low temperature, which should further enhance the secondary thermal cracking reactions.

The propylene yield is strongly affected by both conversion and temperature (Figure 11). At the highest cracking temperature (560 °C), the propylene yield reaches values of 8 wt % at 80 wt % conversion. C<sub>4</sub> olefins present a behavior similar to that of propylene (Figure 11). They are strongly favored by temperature (especially the N-butene) and conversion (monotonically) and can reach yield values of about 14 wt %. The ISO-butene (which is a very important product for TAME production) is about 4.5 wt % on the feed, while the N-butene is about 9 wt %.

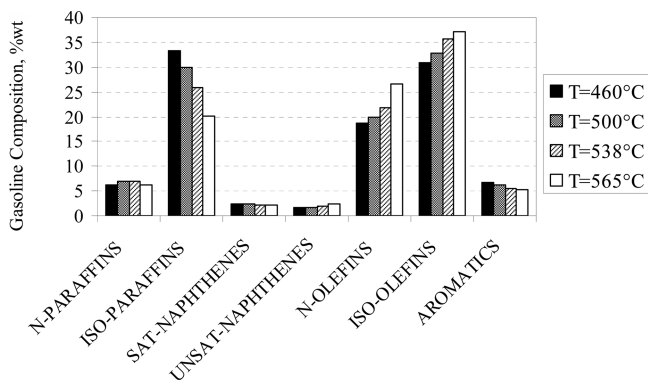
In Figure 12, we present the RON and MON of the gasoline produced at various temperatures. It appears that both octane numbers increase slightly with the temperature. This behavior can be explained by considering the gasoline hydrocarbon composition depicted in Figure 13. This figure shows that, with



**Figure 11.** Effect of the cracking temperature on the LPG olefin yield (catalyst, FCC; 80 wt % conversion).



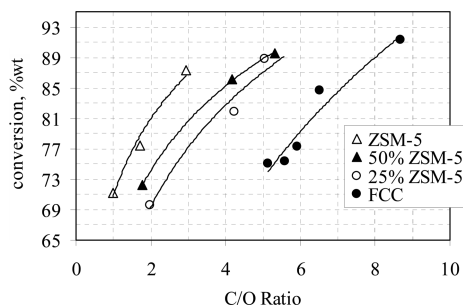
**Figure 12.** Effect of the cracking temperature on the gasoline RON and MON (catalyst, FCC; 80 wt % conversion).



**Figure 13.** Effect of the cracking temperature on the gasoline composition (catalyst, FCC; 80 wt % conversion).

increasing temperature, the gasoline becomes more olefinic in both ISO-olefins and linear olefins. It is known that hydrocarbon cracking is favored at higher temperatures, producing more olefins.

The hydrocarbons that are mainly affected by the increase in the temperature are the ISO-paraffins. As the temperature increases, they undergo further cracking reactions to lighter olefinic and saturated hydrocarbons. However, the main reason is that the increase of the temperature favors the cracking reactions more than the isomerization reactions. Thus, the ratio of ISO-olefins/N-olefins (and ISO-paraffins/N-paraffins) decreases with an increase of the temperature. Moreover, the higher temperature favors the cracking compared with hydrogen transfer, and thus olefins are produced by the cracking of paraffins and they decompose by further cracking. Overall, the higher temperatures favor olefin production. The aromatics are not favored by an increase of the temperature (because of fewer hydrogen-transfer reactions compared with cracking at higher

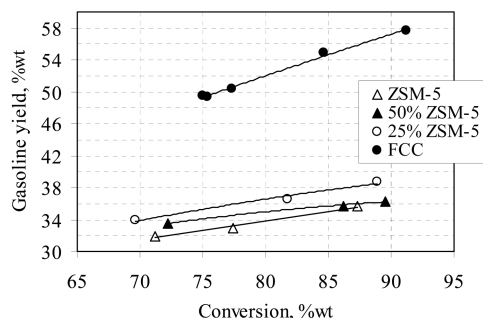


**Figure 14.** Effect of ZSM-5 on the catalyst activity (Wax cracking,  $T = 538$  °C).

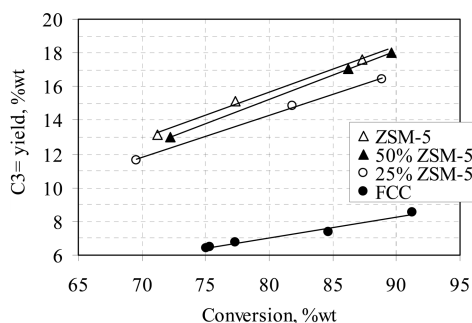
temperatures), and thus aromatics appear to be lower at higher temperatures (as happens with coke).

**3.3. Effect of the ZSM-5 Additive.** In our previous bench-scale studies,<sup>17</sup> it was revealed that the type of catalyst (ZSM-5 vs FCC) has a significant effect on the Wax cracking. For this reason, the effect of a ZSM-5 FCC additive on Wax cracking was also investigated in the present pilot-plant study. Specifically, we tested blends of the FCC catalyst with a ZSM-5 additive (with a very high crystal content) at two concentration levels: 25 and 50 wt %. Experiments with only the ZSM-5 additive were also carried out. In Figure 14, we present the activities of four different catalysts/blends. This figure shows that the presence of a ZSM-5 additive makes the blend more active and, consequently, pure ZSM-5 presents the highest activity of all catalysts, giving conversions of around 70 wt % even at C/O = 1. It appears that the molecules of Wax (linear paraffinic) can enter easily into the small pores of ZSM-5 for cracking. Moreover, the matrix of ZSM-5 should also play an important precracking role for this type of feed. This ZSM-5 behavior is completely different from that observed in the cracking of conventional feeds, where, because of the dilution effect, the presence of ZSM-5 at high concentrations usually reduces the activity of the catalyst.<sup>21,22</sup> The above results are also consistent with the results of Dupain et al.<sup>14</sup> as far as the highest activity of the FCC/ZSM-5 blend is concerned in relation to the FCC catalyst. In the current paper, there is a clear trend that shows that the blend of FCC/ZSM-5 is more active than FCC, while the pure ZSM-5 additive is more active than the FCC/ZSM-5 blend (Figure 14). In the work of Dupain et al.,<sup>14</sup> it was shown that, for the heavy Wax, the Ecat/ZSM5 blend is more active than Ecat (as in the current work); however, the performance of the pure ZSM5 additive is opposite and shows less activity even than Ecat. This difference could be attributed mainly to the different Wax feeds or base catalysts used in the two studies.

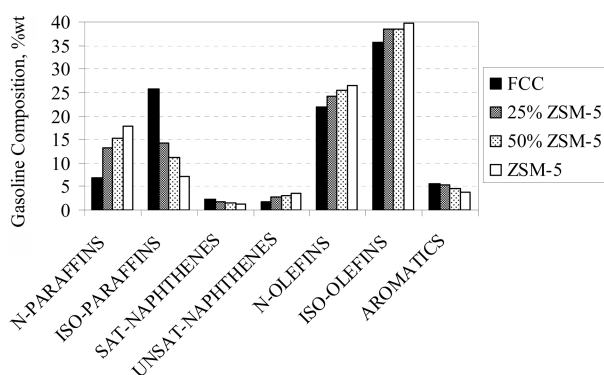
The effect of ZSM-5 addition on an FCC catalyst has been widely demonstrated in the literature.<sup>21,22</sup> It has been shown that the presence of ZSM-5 decreases the gasoline yield by producing more olefins and especially LPG olefins. These effects were also validated in this study using the Wax feed. Figure 15 presents the effect of ZSM-5 on the gasoline yield. The gasoline yield decreases considerably even at a 25 wt % ZSM-5 blend, reaching a minimum value when pure ZSM-5 is used in the inventory of the pilot plant. It is important to note that the incremental decrease of the gasoline yield is very low at ZSM-5 concentrations higher than 25%. As expected, the presence of ZSM-5 causes a high increase in the LPG yield. This effect is presented in Figure 16 for the propylene yield. Figure 16 shows that, even with 25% ZSM-5, the propylene yield is very high, reaching values of 14 wt % (on the feed) at 80 wt % conversion. The highest propylene yield occurs with pure ZSM-5 (up to 18



**Figure 15.** Effect of ZSM-5 on the gasoline yield (Wax cracking,  $T = 538$  °C).



**Figure 16.** Effect of ZSM-5 on the propylene yield (Wax cracking,  $T = 538$  °C).



**Figure 17.** Effect of ZSM-5 on the gasoline composition (Wax cracking,  $T = 538$  °C, 80 wt % conversion).

wt % on the feed at 90 wt % conversion). As with gasoline reduction, the increase of propylene when more than 25% ZSM-5 is used in the inventory is only marginal. It seems that ZSM-5 can have a strong effect on propylene production even at low concentration levels.

The same behavior as that with propylene is also observed (not presented in the figures) with the remaining LPG olefins. With only a ZSM-5 additive, the N-nutene yield reaches values up to about 14 wt %, while the ISO-butene yield reaches up to about 9 wt % on the feed basis. It must also be noted that the presence of ZSM-5 considerably decreases the coke yield. ZSM-5 does not promote the hydrogen-transfer reactions that seem to play an important role in coke production from Wax. Thus, pure ZSM-5 gives coke yields (not presented in the figure) of less than 0.1 wt %.

In Figure 17, we present the gasoline composition (based on PIONA analysis) produced from all catalysts (at 80 wt % conversion). Gasoline analysis (Figure 17) validates our previous discussions that the gasoline produced from Wax cracking contains a very low aromatic content (less than 6%). The presence of ZSM-5 decreases further the aromatics in gasoline.

This is despite the fact that the gasoline from ZSM-5 always has a lower yield compared with the FCC catalyst (zeolite Y).

It must be pointed out that the presence of ZSM-5 always produces a more olefinic gasoline because of the additional cracking of hydrocarbons in the ZSM-5 pores. However, the ISO-paraffins are much lower when more ZSM-5 is present, while the N-paraffins are higher. This is due to the shape selectivity of the ZSM-5 catalysts, which (because of the small pore size) does not permit isomerization of the N-paraffins to the more bulky ISO-paraffins.

#### 4. Conclusions

From the experimental results of the present pilot-plant study, it is shown that the F–T Wax is a very crackable feed (under FCC conditions and catalysts) compared with the more aromatic conventional VGO. This is due to the highly paraffinic nature of this feed. Cofeeding of Wax and VGO is a very flexible solution to a refinery because it can give higher conversions, less coke, and more LPG olefins compared to the VGO operation.

The cracking of Wax hydrocarbons to gasoline hydrocarbons is the main reaction, and thus a high gasoline yield is produced from this feed. The gasoline hydrocarbons are relatively stable, and they do not overcrack even at very high severities. The only exception is gasoline N-olefins, which overcrack at a temperature of 565 °C and at high conversions. This is because the reactivity of the olefinic species in gasoline is much higher than that of the paraffinic species. Besides gasoline, LCO is also produced but in much lower yields. LCO overcracking occurs to a high extent, which indicates the paraffinic nature of this fraction. In general, the F–T Wax molecules are cracked in the acid sites of the catalyst and the formed paraffinic and olefinic products end up in the gasoline fraction (mainly) and in the LCO. LCO molecules can be further cracked to gasoline and LPG components.

A high degree of isomerization reactions takes place in gasoline olefinic and paraffinic molecules, and thus we finally have a high degree of branching in both gasoline olefinic and paraffinic compounds. Hydrogen-transfer reactions also play a role in Wax cracking, leading mainly to aromatic hydrocarbons in the gasoline and to coke. At high conversions, other complex secondary reactions like alkylation and cyclization can also occur, leading also to aromatic compounds in gasoline. The aromatic content in gasoline depends on the type of catalyst and on the operating conditions, but it is always less than 6 wt %. The type of catalyst (zeolite Y vs ZSM-5) plays also a significant role in the selectivity of the FCC products. By a proper selection of the catalyst type and of the operating conditions, a very interesting spectrum of renewable fuels can be produced by this process. ZSM-5 additive is a very active catalyst for this feed, producing high yields of LPG olefins. It produces also a gasoline with many olefins and N-paraffins and very low ISO-paraffinic content.

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