



# Optimized Fuels for Sustainable Transport

Project co-funded by the EUROPEAN COMMISSION FP7  
Directorate-General for Transport and Energy Grant No. 218890

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## Deliverable D4.9

**Report for BTL-naphtha upgrading technologies on pilot scale i) pilot scale hydroisomerization for decreasing CN of upgraded naphtha and ii) production of high added value chemicals through catalytic cracking of FT-naphtha**

Workpackage:	WP4
Deliverable N <sup>o</sup> :	D4.9
Due date of deliverable:	M48
Actual date of delivery:	31/12/12
Version:	Final
Responsible:	CERTH
Authors:	A.A. Lappas, I.A. Vasalos, E. Heliopoulou, E. Heracleous, D. Iatridis
Contact:	angel@cperi.certh.gr
Dissemination level:	PU

## **D4.9. A) Validation of naphtha hydro-isomerization on pilot scale using the best catalyst synthesized in CERTH and tested on bench scale**

### **A1. INTRODUCTION**

In the deliverable D4.4 we investigated on bench scale two (2) different upgrading options for the BtL naphtha. We concluded that the isomerization technology is the best in the case that a decrease in the cetane number of the BtL-naphtha is necessary. It is well known that with the classical hydroisomerization process in the refining industry, the normal paraffins of the light straight naphtha (C<sub>5</sub>-85°C) can be converted into their isomers (isomerate product), resulting in an increase in RON and MON but a decrease in CN due to lower cetane values of the branched alkanes compared to n-alkanes. Our bench scale studies showed that even with a commercially available catalyst we can decrease the CI of a BtL naphtha till about 12 units depending on the operating conditions used in the Hydroisomerization process. Moreover, in D.4.4 we proved that with a catalyst synthesized in CPERI during OPTFUEL (Pt/ZSM-5) we can achieve a satisfactory isomerization with the benefit that this catalyst is more tolerant to H<sub>2</sub> and S compared to the commercial one.

In this deliverable we scaled up this process using a pilot plant unit, the new catalyst and a large quantity of an artificially naphtha that simulates the BtL naphtha composition. The objective was to prove this technology on pilot scale and to be able to deliver large quantities of upgraded BtL-naphtha for single cylinder tests.

### **A2. EXPERIMENTAL**

#### **A2.1 The pilot-scale isomerization unit**

The hydroisomerization tests were performed on the high pressure pilot scale test unit of CPERI (Figure A1).



**Figure A1** : View of CPERI's high pressure pilot scale isomerization test unit

The unit consists of two fixed bed reactors (45.72 cm length x 2.8 cm ID) which can operate in series or independently one from the other, for up or down flow. The reactors can operate at temperatures up to 550°C and pressures up to 150 atm. The feed system includes three

independent gas feed modules and one liquid feed module with all necessary equipment. The mass of catalyst put in each reactor is 20 gr. For the better operation of the unit the catalyst is mixed (diluted), inside the reactor, with a non active material ( $\alpha$ -alumina). This dilution improves the flow pattern by increasing the liquid hold up and residence time distribution. Moreover, the inert material helps for achieving isothermal condition in the two reactors during the experiments. According the above, the loading of catalyst and  $\alpha$ -alumina mixture is very important for the correct operation of the unit and it was performed with a special procedure developed in CPERI.

Before the start of the experiments, the catalyst is calcined for two hours at 425°C and then gets sulfided by a H<sub>2</sub>/H<sub>2</sub>S gas mixture at 260°C so that the catalyst's metallic oxides convert to sulfide ones. For the tests both reactors were used in down flow operation. The reactors' outlet is cooled and led to a separator where the gas and liquid parts are separated. The level of the liquid product in the separator is automatically regulated. The gases exiting the separator pass through a NaOH trap so that the produced H<sub>2</sub>S is removed and then through a wet test meter. The pilot plant unit is fully automated and functions by means of a computer connected with an automatic control system. The computer receives all the plant's signals and executes all the control and adjustment actions, so that the unit can operate for a long period of time at unattended operation.

## A2.2 Catalytic material

Based on results from Del. 4.4 we selected the Pt/ZSM-5 as the best catalyst for BtL naphtha isomerization since:

- It can reduce till 12 units the CI even with the heaviest naphtha tested
- It can give upgrading naphtha yield more than 97%wt compared to BtL naphtha
- It is more tolerant to impurities compared to the commercial samples

For the purpose of this deliverable we should synthesize a large amount (120 gr) of Pt/ZSM-5 catalyst for pilot scale tests using the same recipe as in Del. 4.4. Specifically we used the following steps:

- Commercial Zeolyst ZSM-5 material, conversion to H<sup>+</sup>-form: Calcination 500°C/3h/synthetic air
- Dry impregnation with H<sub>2</sub>PtCl<sub>6</sub> as the precursor salt. Drying and calcination at 400°C for 3hs under air atmosphere
- Catalyst Characterization including the following:

The platinum content of all samples was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with a Perkin-Elmer Plasma 40 instrument. Surface areas of the samples were determined by N<sub>2</sub> adsorption at 77K, using the multipoint BET analysis method, with an Autosorb-1 Quantachrome flow apparatus. Prior to the measurements, the samples were dehydrated in vacuum at 250°C overnight. Pyridine adsorption –FTIR measurements were used for acidity determination. All the samples were finely ground in a mortar and pressed in self-supporting wafers ( $\approx 15$  mg/cm<sup>2</sup>). The wafers were placed in a homemade stainless steel, vacuum cell, with CaF<sub>2</sub> windows. High vacuum is reached by the means of a turbomolecular pump and a diaphragm pump placed in line. The infrared cell was equipped with a sample holder surrounded by a heating wire for the heating steps and connected to the vacuum line, which is also heated in order to avoid pyridine condensation or its adsorption on the walls. Before IR analysis, all samples were heated at 450 °C under high vacuum (10<sup>-6</sup> mbar) for 1 h in order to desorb any possible physisorbed species (activation step). All spectra were collected at 150 °C in order to eliminate the possibility of pyridine condensation. Initially, the reference spectrum of the so-called activated sample is collected. Then adsorption of pyridine is realized at 1 mbar by equilibrating the catalyst wafer with the probe vapour, added in pulses for 1 h.

**Table A1:** Characterization results of the parent ZSM-5 material received from Zeolyst

<i>Support</i>	<i>SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio</i>	<i>Zeolite SA, m<sup>2</sup>/g</i>	<i>Zeolite micro-porosity, cm<sup>3</sup>/gr</i>	<i>Brönsted acid sites (μmol/g)</i>	<i>Lewis acid sites (μmol/g)</i>	<i>Total Acidity (μmol/g)</i>
H-ZSM-5	23	417.69	0.1429	477.36	113.44	590.81

**Table A2:** Characterization results of the optimum Pt/ZSM-5 material synthesized in CPERI

<i>Catalyst</i>	<i>Pt loading (ICP), ppm</i>	<i>Support</i>	<i>Brönsted acid sites (μmol/g)</i>	<i>Lewis acid sites (μmol/g)</i>	<i>Total Acidity (μmol/g)</i>
Pt/ZSM-5	1095±65	H-ZSM-5	414.25	125.9	540.15

### A2.3 Feedstock

For the pilot scale validation of this upgrading technology it was not possible to use the existing BtL sample due to the very limited amount for pilot scale studies. Thus, for this study we used the heaviest naphtha B2, which was artificially synthesized from pure components (50 lit) and fully characterized. The main properties and the chemical composition of this feed are tabulated in Table A3. The Cetane Index (CI) of the feed is also reported. As there is no commercially available software for CI estimation on naphthas, the estimation was performed with a method developed in CPERI after communication with IFP, based on the individual contribution of each hydrocarbon in the feed. The same method was used for the estimation of the CI of the isomerization products.

**Table A3:** Properties and composition of the tested feed

<b>Feed</b>	<b>Heavy – B2 (C<sub>5</sub> – C<sub>10</sub>)</b>
Density, g/cm <sup>3</sup>	0.69
Cetane Index	50.8
<b>Composition, wt%</b>	
Total Normal Paraffin	65.6
Total Iso Paraffin	34.4
C5 Normal Paraffin	4.94
C6 Normal Paraffin	12.05
C7 Normal Paraffin	15.33
C8 Normal Paraffin	15.65
C9 Normal Paraffin	11.71
C10 Normal Paraffin	5.98
C5 Iso Paraffin	3.08
C6 Iso Paraffin	6.21
C7 Iso Paraffin	-
C8 Iso Paraffin	25.04
C6 Naphthene	-
C6 Aromatic	-

## A3. EXPERIMENTAL RESULTS AND DISCUSSION

### A3.1 Operating procedure

The optimum operating conditions concluded from Del. 4.4 were also applied in this study. Specifically the following conditions were applied in the pilot plant:

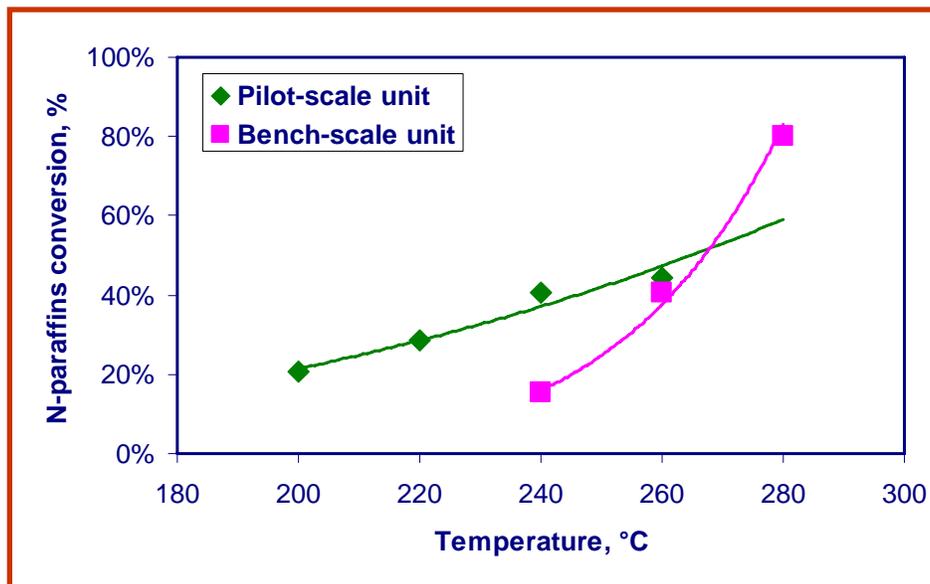
- Reaction pressure: 30 bar
- Catalyst mass: 50 gr
- Reaction temperature: 200-260°C
- WHSV: 2.2 h<sup>-1</sup>

- Sampling: 8h under steady state conditions
- Product analysis → Liquids: PIANO method, Gases: GC
- Pretreatment: 1 week Steady state run: 1 week

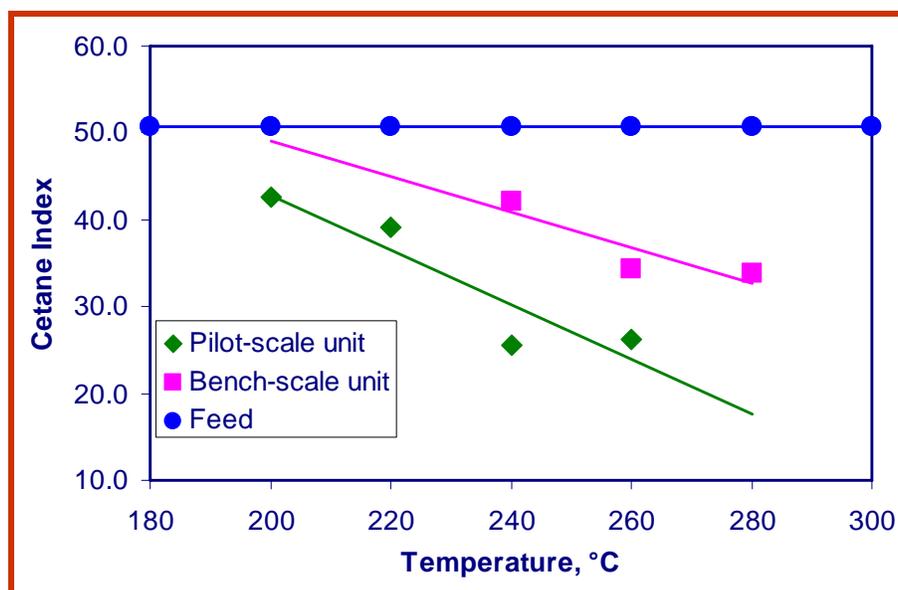
The steady-state activity measurements were taken after at least 8 h on-stream, collecting and analyzing both a liquid and a gaseous product sample. The liquid samples were analyzed with PIANO analysis, while the composition of the reaction off-gases was detected with a GC.

### A3.2 Scale effects on catalyst activity and Cetane Index

Fig. A2 presents the effect of temperature on n-paraffins conversion for the two test units (pilot and bench-scale), whereas in Fig. A3 the cetane index of the isomerate product compared to that of the heavy naphtha B2 versus temperature for both units is presented.



**Figure A2** : N-paraffins conversion vs temperature (P=30 bar, WHSV=2.2 h<sup>-1</sup>, H<sub>2</sub>/HC=0.4)



**Figure A3** : Cetane Index vs temperature (P=30 bar, WHSV=2.2 h<sup>-1</sup>, H<sub>2</sub>/HC=0.4)

From the above results it is clear that the performance of the CPERI synthesized Pt/ZSM-5 catalyst was fully validated on pilot scale. Of course the Pt/ZSM5 catalyst has a better performance on pilot scale compared to bench scale. The above results concluded that hydroisomerization of the heavy naphtha (model feed B2) is feasible on pilot scale at even lower temperature compared to bench scale (targeting to the same CI reduction)

### A3.3 Scale effects on product distribution

As can be clearly observed in Fig. A4, the pilot scale unit at 220°C gives more iso-C<sub>7</sub>, C<sub>6</sub>, C<sub>5</sub> and C<sub>4</sub> compared to bench scale at 260°C. Furthermore, bench scale at 260°C gives more iso-C<sub>8</sub> compared to pilot scale at 220°C. Iso-C<sub>4</sub> olefins are observed on both scales.

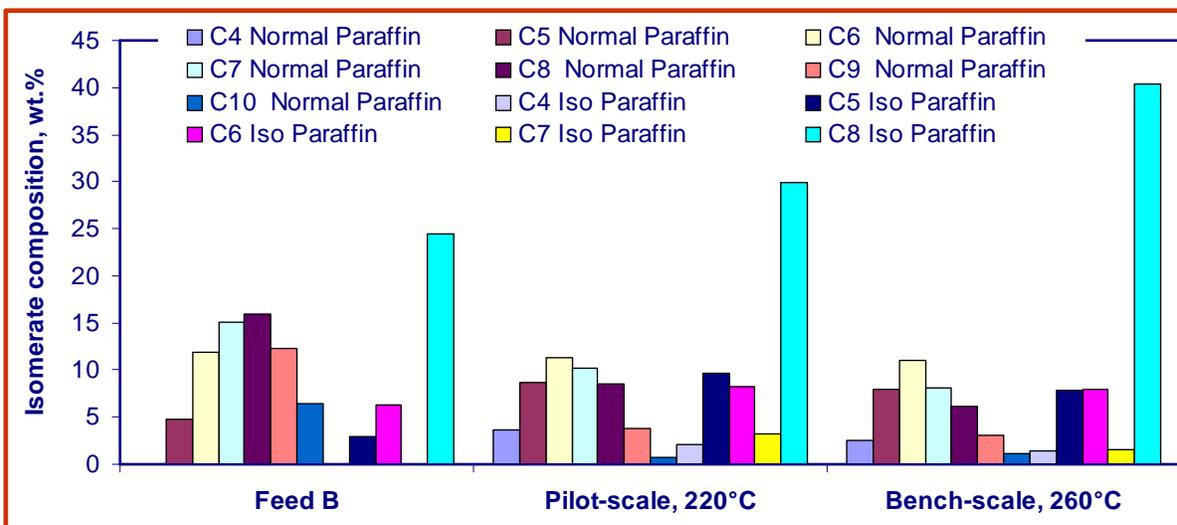


Figure A4 : Isomerate product distribution compared to that of the heavy naphtha B2

### A3.4 Temperature effects on product distribution

The effect of hydroisomerization temperature ranging from 200-240°C on product distribution is presented in Figure A5.

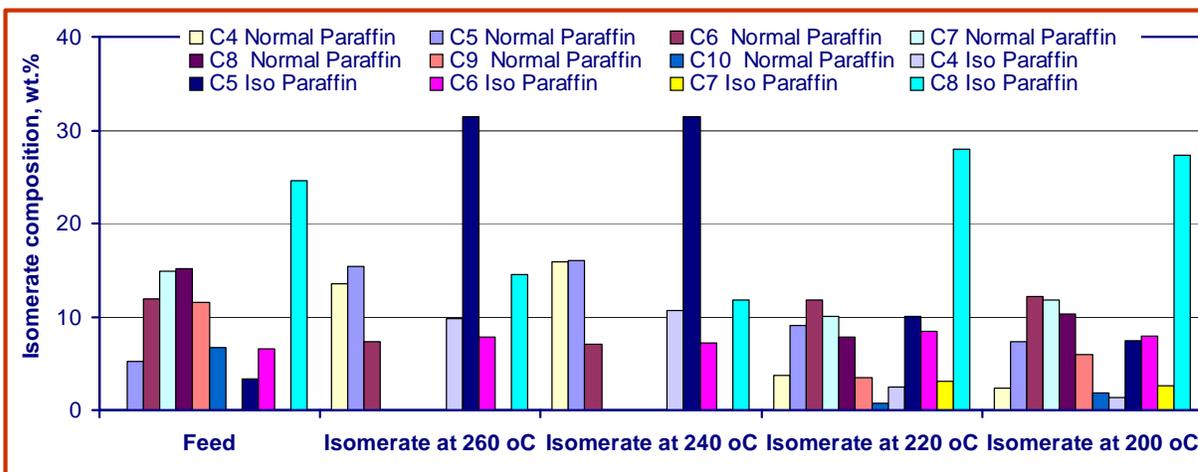


Figure A5 : Effect of reaction temperature on isomerate product distribution for the pilot scale test

From the pilot-scale evaluation at different temperatures it is concluded that the reaction temperature strongly affects the conversion/isomerization of the n-paraffins. A reaction

temperature equal to  $T=220^{\circ}\text{C}$  seems to be the optimum temperature for pilot scale hydroisomerization of the heavy naphtha B2. The isomerate product has an iso-paraffin content of about 55%wt., while the used heavy naphtha had correspondingly 34%wt. The dry gases were less than 1%wt on feed. The n-C<sub>4</sub> formation was very low (about 3.8%wt)

#### **A4. CONCLUSIONS**

The pilot scale Hydroisomerization tests performed in this deliverable fully validated the results from the bench scale tests of Del. 4.4. The pilot plant experiments were performed at the same conditions as the bench scale tests with a capacity of 10 liters of feed/hour. Scale effects have been investigated on catalyst activity and cetane index as well as on isomerate product distribution. The effect of reaction temperature on isomerate product distribution was also studied. From the experimental results the following conclusions can be derived:

- The upgrading scheme was validated on pilot scale that can reduce (up to about 25 units) the CI of an (artificial) heavy naphtha, which simulates the commercial BtL naphtha
- Hydroisomerization gives high naphtha yield and aromatic minimization
- The Pt-ZSM-5 catalyst has a better performance on pilot scale compared to small scale with the heavy B2 naphtha
- Pt-ZSM-5 is active for the conversion of heavier (>C<sub>6</sub>) components exhibiting high selectivity and low cracking tendency

Figure A2 shows the conversion of n-paraffins in the bench scale and pilot plant test units as a function of temperature. Similar results were obtained in the two units, albeit a 40°C temperature difference for achieving the same conversion levels. This outcome is very promising and ensures that the hydro-isomerization of naphtha can be easily up-scaled to pilot plant scale to produce the required amounts of test fuel for the engine tests.

## **D4.9. B) Production of high added value chemicals through catalytic cracking of FT naphtha**

### **B1. INTRODUCTION**

The objective of this work was the production of high added value chemicals from BtL Naphtha through catalytic cracking on pilot scale. The very small available quantity of BtL naphtha was used on bench scale tests and this work was presented in Del. 4.7. In this deliverable was proved that the BtL naphtha can be used for high added value chemicals production through catalytic cracking and especially for ethylene, propylene and butylenes production. For application of this technology on pilot scale sufficient quantities of BtL naphtha were not available. For this reason a work was carried out in CPERI for identification of a refinery naphtha stream that could simulate (as much as possible) the composition of the available BtL naphtha.

The work performed in CPERI for the identification of the best refinery naphtha stream included the collection of all naphtha streams (from a conversion refinery with a high complexity index) and the analysis of these naphthas (in CPERI laboratory) using a PIANO GC method. The criteria for this selection was i) the refinery naphtha to have the less aromatic and olefins content since BtL naphtha has with almost zero aromatics and olefins, ii) the boiling range to be as close as possible to BtL naphtha iii) the composition of the other hydrocarbons (paraffins and naphthenes) to be as similar as possible to BtL naphtha. From this work and for the specific refinery it was concluded that the naphtha stream to the reformer unit simulates better the BtL naphtha composition. For the specific refinery of this study the stream has an aromatic content of 11%wt, zero olefins and n-paraffins=24%wt, i-paraffins=29%wt, Sat-naphthenes=36%wt. CPERI results from this study was in full agreement with internal CONCAWE data. For this reason we selected to use this naphtha stream for pilot plant studies regarding the catalytic cracking technology of BtL naphtha for high added value chemicals production. CONCAWE worked with a refinery for the supply of this naphtha stream and thus we name this refinery naphtha as naphtha or refinery naphtha.

### **B2. EXPERIMENTAL**

#### **B2.1 Naphtha Feed**

One barrel of the refinery naphtha feed was sent by Concawe to CPERI/CERTH for the pilot plant studies. This feed had an API value equal to 54.6, a specific gravity of 0.7604 and a sulfur content of 0.3 ppmw. The simulation distillation data of this naphtha is given in Fig. B1. It seems that this naphtha has an IBP of about 55°C and a FBP of 185°C. The PIANO analysis of the naphtha is presented in Fig. B2. This naphtha consists mainly of saturated naphthenes (about 43%wt), isoparaffins and normal paraffins. The olefins are very low while the aromatics are 20%wt. By comparing this naphtha with the BtL Naphtha (used in Del. 4.7) it seems that BtL naphtha contains only n- and iso-paraffins with no aromatics while refinery naphtha contains 20% aromatic and 43% saturated naphthenes. Moreover, much less n-paraffins exists in the refinery naphtha. Unfortunately the aromatic content of this naphtha is higher compared with the naphtha used in the preliminary CPERI study (as discussed in the introduction) In Fig. B2 we also present the carbon distribution of the hydrocarbons in this naphtha. It seems that it contains mainly C7-C9 compounds with lower C6 and C10.

#### **B2.2 Catalysts of the study**

Two commercially available catalytic materials used in the present study: a low activity Ecat with low metals (TSA=178 m<sup>2</sup>/g, ZSA=58 m<sup>2</sup>/g, UCS=24.26Å) and a commercial catalyst (CAT-B) selective for maximum olefins production. This catalyst was selected from the previous bench scale studies presented in Del. 4.7.

### **B2.3 Experimental unit. The FCC pilot plant**

All experiments of this study were carried out in CPERI FCC pilot plant unit. 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 (Fig. B3 and Fig. B4) operates in a full catalyst circulation mode with continuous regeneration and consists of a riser reactor (7mm ID and about 9 m height), the stripper, the lift line and a fluid bed as the regenerator (78mm ID). The catalyst circulation is achieved with two slide valves and it is controlled in a similar way as 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, the flue and cracked gases and the total liquid product yield are measured. From the total liquid product the yields of gasoline, LCO, HCO are determined using 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 GC's, 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).

## **B3. EXPERIMENTAL RESULTS AND DISCUSSION**

### **B3.1 Cracking refinery naphtha at various temperatures for maximizing C<sub>3</sub><sup>=</sup> production (Ecat)**

In Fig. B5 we present the high added value chemicals (ethylene, propylene and butylenes) produced from the cracking of the refinery naphtha at three temperatures (538°C, 566°C, 593°C). It seems that by increasing the cracking temperature all chemicals yields increase. At the highest temperature we can achieve C<sub>3</sub>H<sub>6</sub> up to about 5.5%wt (on naphtha), slightly less nC<sub>4</sub>H<sub>8</sub> (4%wt) and even less C<sub>2</sub>H<sub>4</sub> (about 1.1%wt). The small-scale (ACE) data using the same catalyst at 538°C and the real BtL naphtha showed that the chemicals produced are the following: Propylene=2.6%wt, C<sub>4</sub>H<sub>8</sub>=2.0%wt, C<sub>2</sub>H<sub>4</sub>=0.25%wt. By comparing these data with Fig. 5 it seems that the results are consisted. In Fig. B6 we present the low value products from this process (propane and dry gases). Higher temperatures produce more dry gases and higher yield of propane. However, both are less than 2.5%wt even at the highest temperature of 593°C.

The conversion of the refinery naphtha is given in Fig. B7 as a function of temperature. Higher temperatures give higher conversion but in general the conversion is about 20% due to the high aromatic content of this naphtha. This means that almost 80%wt of the original naphtha remains as unconverted naphtha that should be used for other applications. The hydrocarbons yields of the remaining (unconverted) naphtha are given in Fig. B8. It seems that there is an increase (production) in the aromatics from 20% to about 24% that is independent of the cracking temperature. The n-paraffins and the iso-paraffins are also not affected significantly and they start to crack only at the highest temperature (but in low extent). The saturated naphthenes that were the dominant components decrease and it seem that they are the main hydrocarbons that crack to LPG.

### **B3.2 Pilot scale using CAT-B from the bench scale evaluation**

In the second part of this work the CAT-B was used for cracking the refinery naphtha. CAT-B was selected from previous bench scale (ACE) data using the BtL naphtha (results presented in Del. 4.7). In Fig. B9 we present the bench scale results (ACE data) using the CAT-B and the BtL naphtha. The excellent performance of this catalyst with the BtL naphtha was recognized since it produced a significant amount of high added value chemicals.

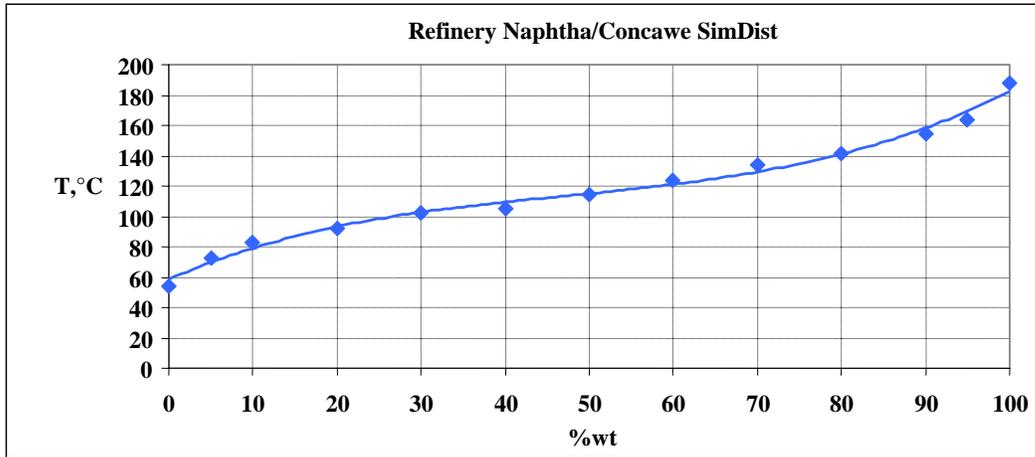
In Fig. B10 we compare the yields of propylene and n-butenes with the Ecat (from the previous paragraph) and the CAT-B. It is clear that indeed the CAT-B is more selective in high added value product compared to Ecat. However, the cracking performance of the Refinery naphtha is not comparable to BtL naphtha regarding the yields of these products. By comparing Fig. B9 and Fig. B10 it seems that the refinery naphtha gives about 7%wt propylene compared to 11% of the BtL naphtha. For nC<sub>4</sub>H<sub>8</sub> the difference is lower (3.5%wt vs. 4%wt at 593°C). For C<sub>2</sub>H<sub>4</sub> the difference is higher (1.8%wt vs. 6%wt). It seems that for the lighter products (ethylene and propylene) the difference between the two naphthas is much higher compared to the heavier products (butylenes).

The remaining naphtha after the cracking at 538°C with the CAT-B was about 78%wt. This value is similar to that obtained by the Ecat (Fig. B7). From the PIANO analysis of this naphtha it seems that the cracking process gives a very low production of aromatics (22.6% from the 20% of the original naphtha). The saturated naphthenes are the hydrocarbons of the original naphtha that undergo cracking since from the 4e% of the original naphtha we achieve 23.6%wt yield in the remaining naphtha. Normal and iso paraffins are affected less by the cracking process.

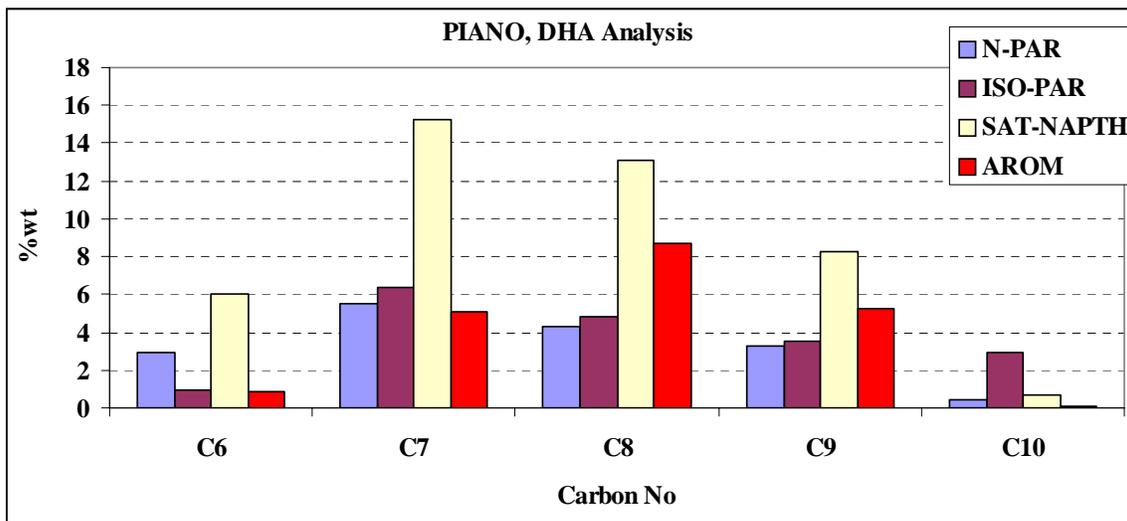
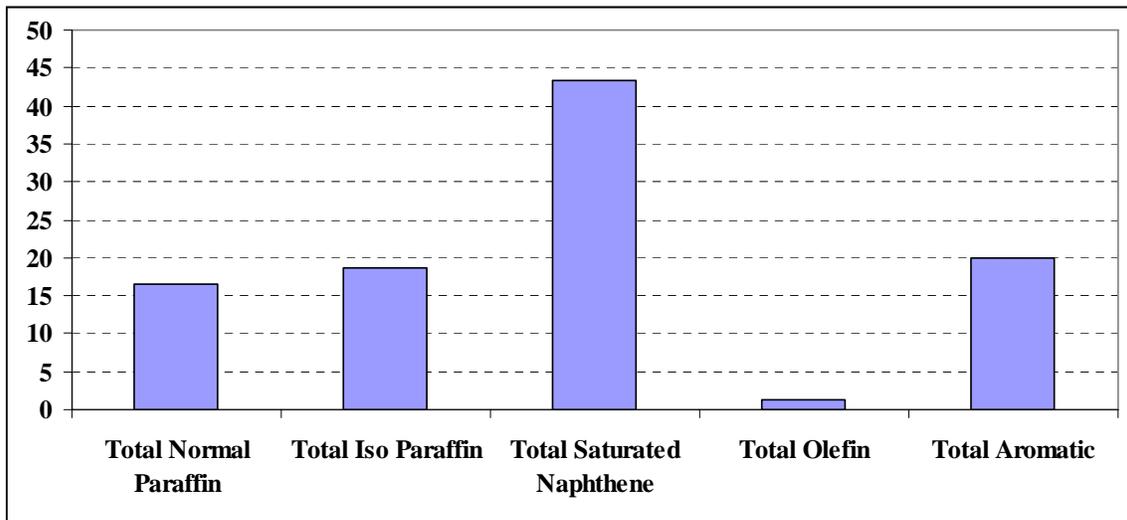
#### **B4. CONCLUSIONS**

In this work pilot plant studies were carried out in order to validate the upgrading technology of the BtL naphtha catalytic cracking towards production of high added value chemicals. Unfortunately sufficient quantities of a BtL naphtha for pilot scale studies were not available. For this reason and after a preliminary study we selected a refinery naphtha stream with composition as close as possible to the BtL naphtha. However, even with this refinery stream (supplied by the refinery) significant differences exist between the two naphthas (for example the refinery naphtha has 20%wt aromatic while the BtL zero).

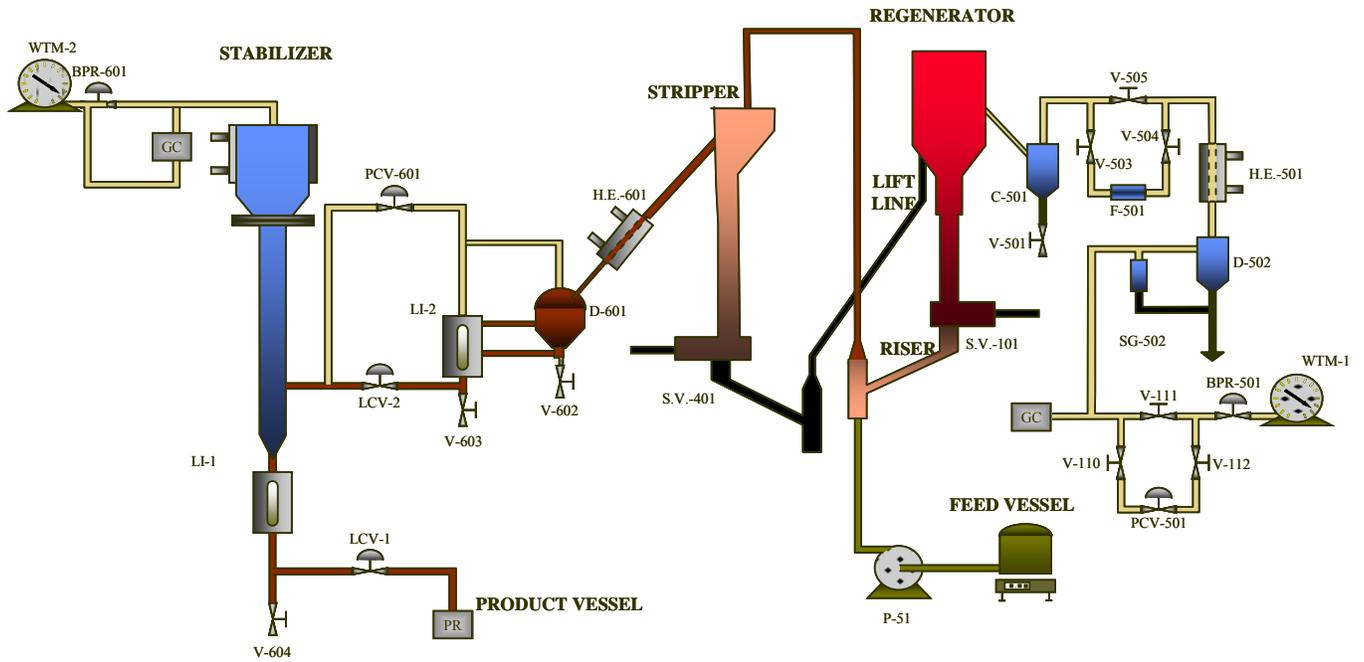
For the work we used a fully circulating FCC pilot plant, two different catalysts and a range of cracking temperatures trying to produce high added value chemicals like ethylene propylene and butylenes. It was shown that Refinery naphtha produces similar results to BtL naphtha when the Ecat was used. However, using a LPG olefins selective catalyst (CAT-B) less olefins (ethylene and propylene) were produced compared to BtL naphtha cracking. Thus, at 593°C cracking temperature the refinery naphtha produced about 7%wt propylene while the BtL about 11%wt. Of course part of this difference may attributed to the different unit (small scale vs. pilot scale) however, the different composition of the two naphthas and especially the high content of the aromatics definitely affect the cracking performance of the two naphthas.



**Figure B1:** SimDist of Refinery Naphtha Feed



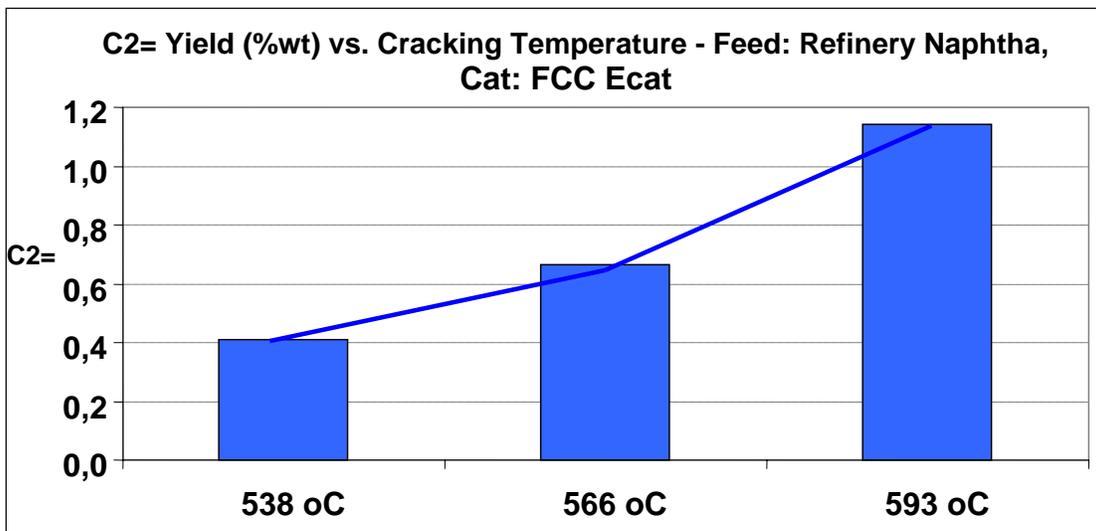
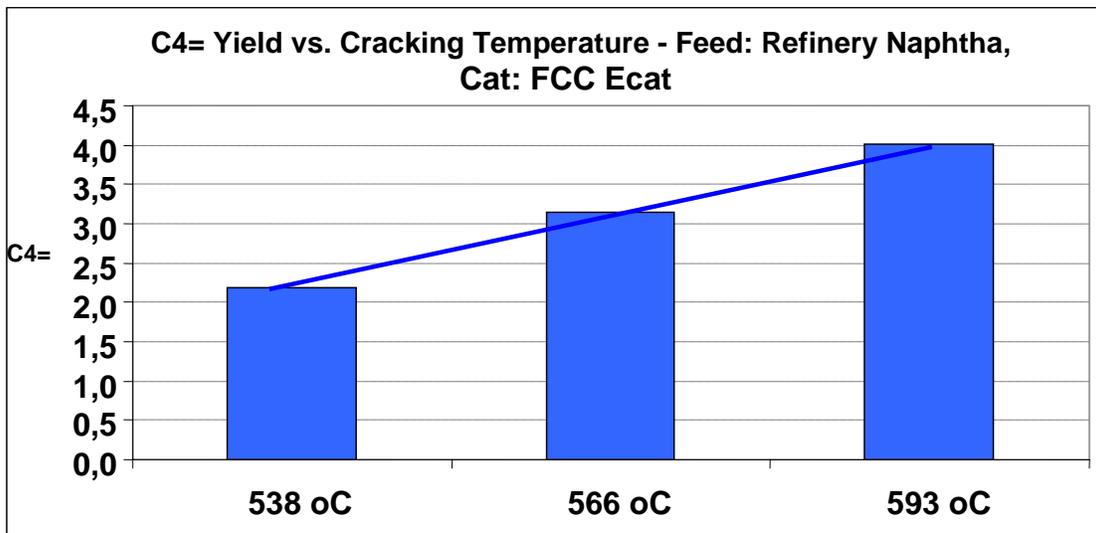
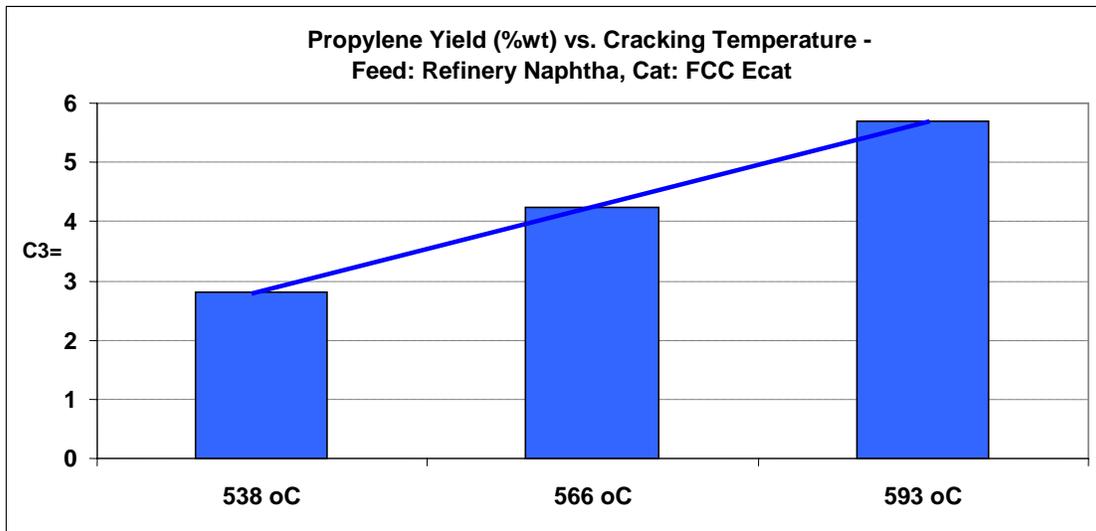
**Figure B2:** Refinery Naphtha Analysis (%wt on naphtha)



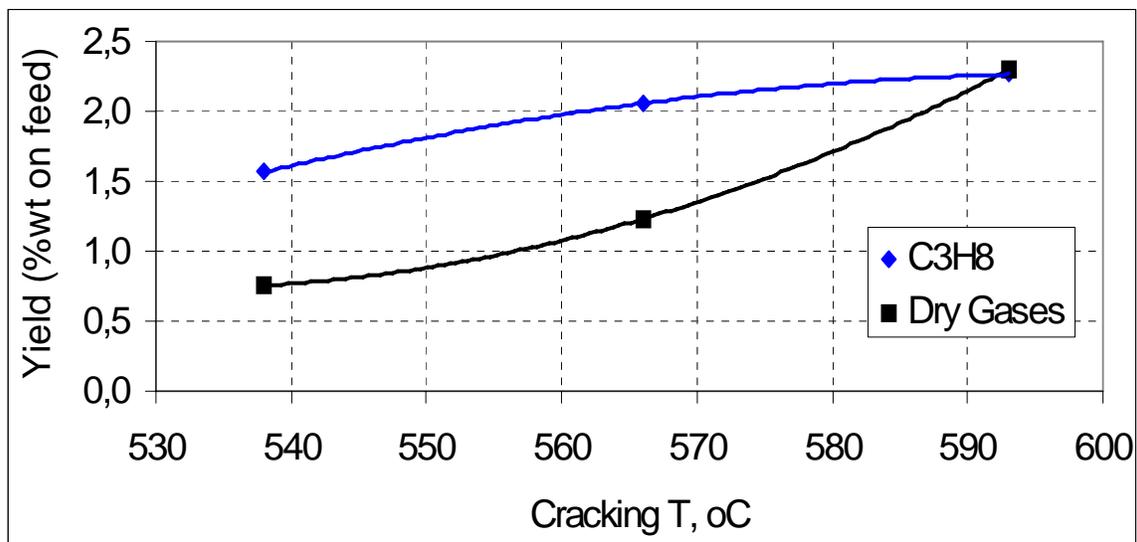
**Figure B3** : Schematic diagram of the FCC pilot unit



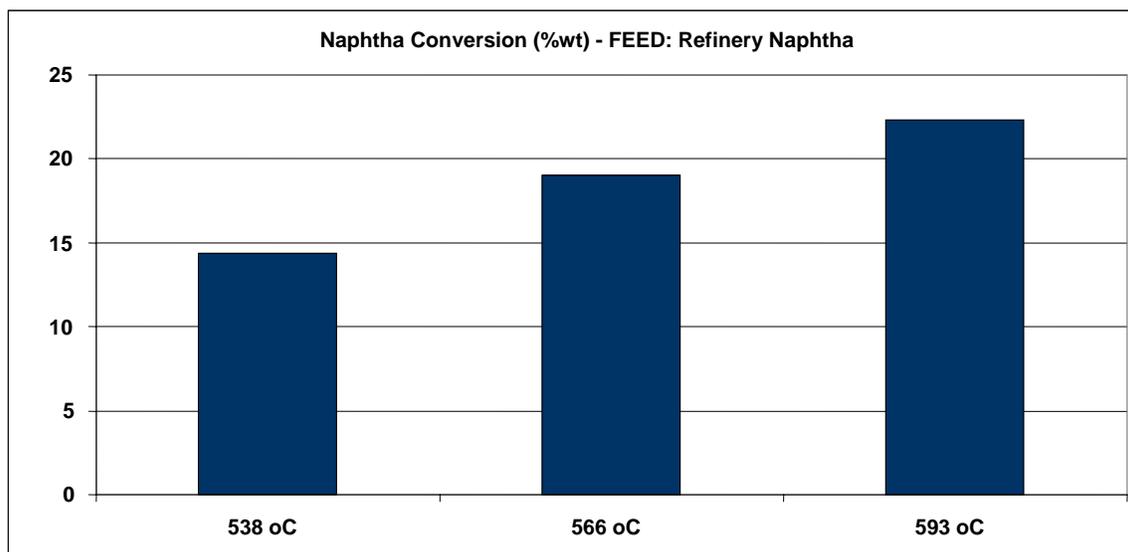
**Figure B4** : Picture of the FCC pp unit



**Figure B5:** Cracking Refinery Naphtha at various T for maximizing  $C_3$ ,  $C_4$  and  $C_2$  production



**Figure B6** : Cracking Refinery Naphtha at high temperatures: Propane and dry gas yields



**Figure B7**: Cracking Refinery Naphtha at various temperatures: naphtha conversion

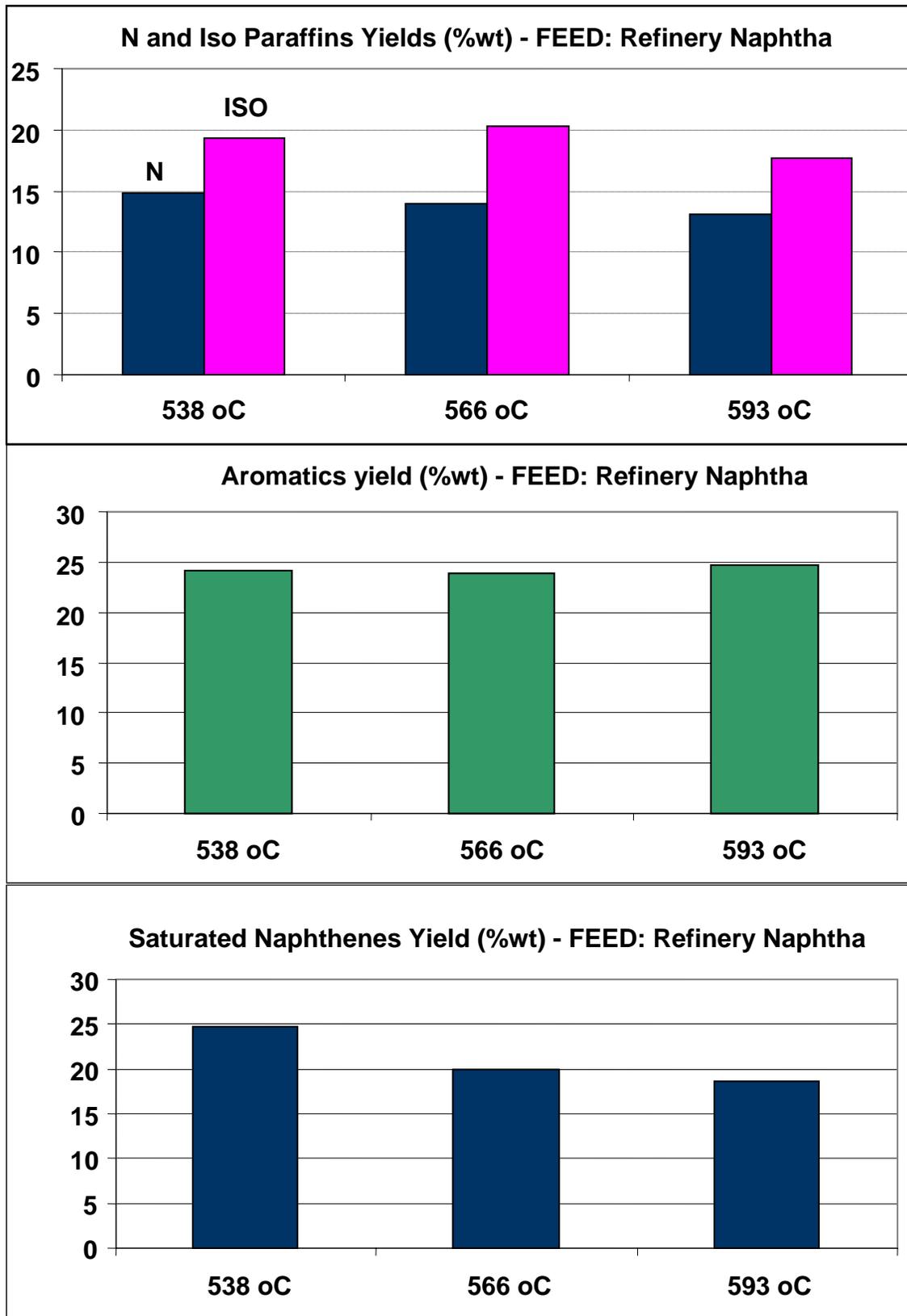


Figure B8: Cracking Refinery Naphtha: C<sub>5</sub>+ HC yields

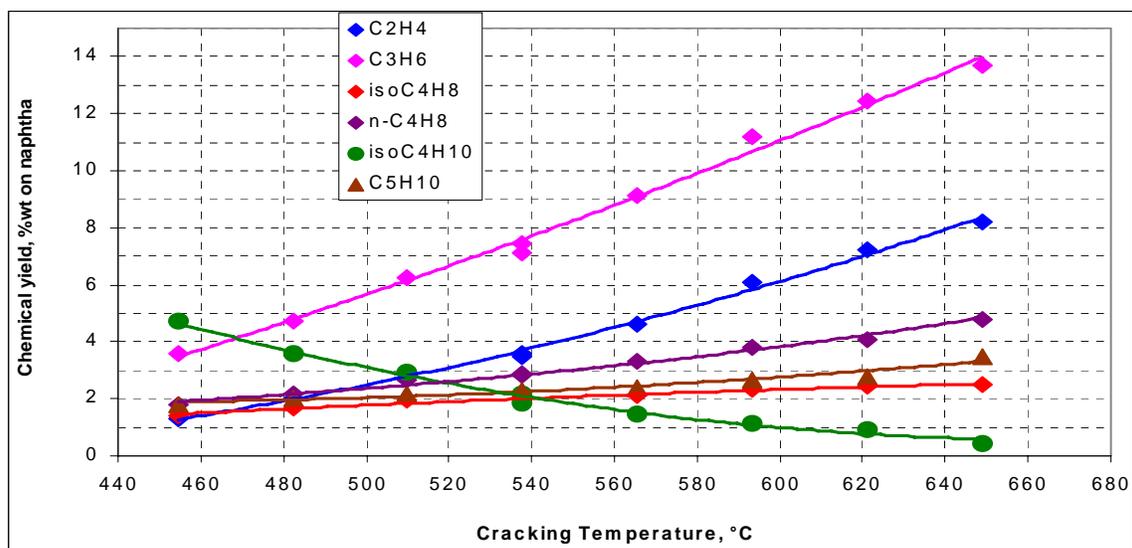


Figure B9 : Previous work with CAT-B with BtL naphtha on bench scale

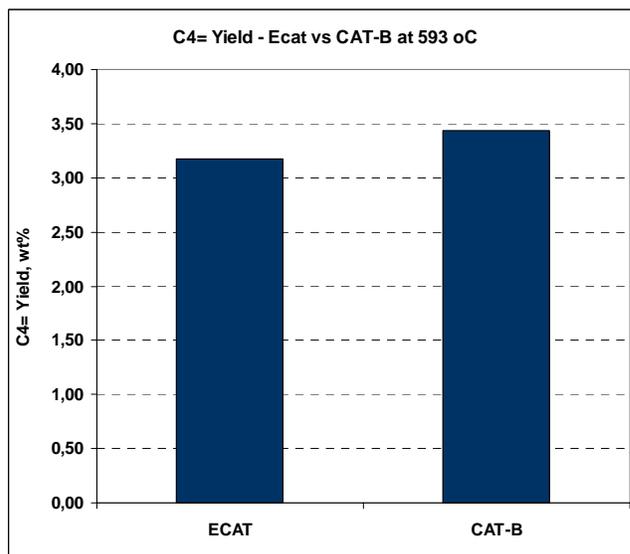
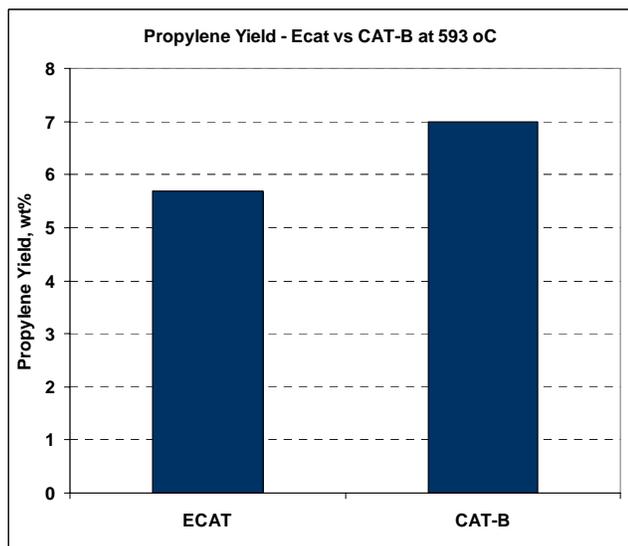


Figure B10 : Pilot scale Ecat vs CAT-B comparison