Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 51 (2) 80-90, 2009

UPGRADING OF DELAYED COKER LIGHT NAPHTHA IN A CRUDE OIL REFINERY

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Received January 28, 2009, accepted April 15, 2009

Abstract

The paper discusses the details and results of the industrial scale experiments, motivated by the constraint of integrating the low quality delayed coker light naphtha fraction stream into refinery. Practically all systems of the refinery processing structure were tested, looking for a suitable location for the further treatment of this light naphtha fraction. DCLN was processed in four different plants of the refinery: FCC unit, AV distillation unit, gas oil hydrotreater and finally in a revamped two-stage naphtha hydrotreating unit. As a final solution, blend of coker naphtha and straight run naphtha was hydrotreated in two consecutive reactors over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalyst respectively. A valuable feedstock, which is virtually free of diolefins, silicon and sulphur was produced from the inferior DCLN stream.

Keywords: coker naphtha; HDS; diolefin saturation; silicon removal.

1. Introduction

As the crude oil demand of the world constantly increases, extraction of heavier crude oils becomes more and more necessary. Also, higher fraction of the low-value residual oil needs to be converted into valuable hydrocarbon stocks (gasoline, Jet fuel, gas oils, lube oils, etc.). Therefore, the significance of the residue conversion technologies has been increasing in the past decade. These technologies can significantly enhance the conversion level of a petroleum refinery. Thermal cracking (visbreaking, thermal cracking, coking, etc.) is one of the major residue conversion technologies, products of which contain large amount of unsaturated hydrocarbons like olefins and diolefins as well as sulphur and nitrogen, among many others. Although, the average share of coker naphtha fractions in the refinery gasoline pool is only about 1-2 vol.%, their sulphur content might be in the magnitude of several per cents, i.e. they can largely contribute to the sulphur content of gasoline pool.

Authorities are world-wide forcing the petroleum companies to reduce the sulphur content of fuels below 50, 30 or 10 mg/kg. According to the Directive 2003/17/EC of the European Parliament and Council, for example, member states of the European Union have to ensure that the sulphur content of the marketed engine gasoline does not exceed a maximum of 10 mg/kg by 2009.

Delayed coking is one of the most wide-spread residue conversion technologies. It is a thermal cracking process used in petroleum refineries to upgrade and convert petroleum residuum (bottoms from atmospheric and vacuum distillation of crude oil) into liquid and gas product streams leaving behind a solid concentrated carbon material, petroleum coke. A fired heater with horizontal tubes is used in the process to reach thermal cracking temperatures of 485 to 505°C. With short residence time in the furnace tubes, coking of the feed material is thereby “delayed” until it reaches large coking drums downstream of the heater. Three physical structures of petroleum coke: shot, sponge, or needle coke can be produced by delayed coking. These physical structures and chemical properties of the petroleum coke determine the end use of the material which can be burned as fuel, calcined for use in the aluminium, chemical, or steel industries, or gasified to produce steam, electricity, or gas feedstocks for the petrochemicals industry.

Integration of DCLN (delayed coker light naphtha) into the processing structure of a petroleum refinery is a big challenge due to its composition and properties (Table 1).

Table 1. Typical characteristics of delayed coker light naphtha fractions

Characteristics	**Values**
Density (15°C), g/cm^3	0.650-0.680
Sulphur content, mg/kg	5000-20000
Nitrogen content, mg/kg	50-300
Research octane number (RON)	80-90
Motor octane number (MON)	70-80
Hydrocarbon composition, vol%	
paraffins	40-50
olefins	30-50
diolefins	1-2
naphthenes	5-10
aromatics	0.5-2
Distillation (ASTM D86), °C	
initial boiling point	25-35
95 vol%	65-80
final boiling point	75-85
Bromine number, g Br/100g	20-100
Silicon content, mg/kg	1-20

Very few studies are published about the upgrading of coker naphtha fractions. Besides direction to the gasoline blender, which is not a real option due to the tough gasoline specifications, there are basically three opportunities: A) injection of DCLN into the riser of the fluid catalytic cracking unit B) selective diolefin saturation/silicon adsorption prior to hydrodesulphurization C) co-processing of the DCLN with fluid catalytic cracker's (FCC) gasoline fraction.

A number of papers were published about the co-cracking of coker naphtha with heavier hydrocarbon fractions. For instance, Fernandez et al investigated the catalytic cracking of the mixture of heavy coker naphtha and vacuum gas oil (VGO) in a bench scale reactor, which is a simulator of an FCC riser[1]. They concluded, that this method might be a reasonable approach to increase gasoline yield, although a trade-off with product quality has to be considered. Coke yield were not higher than the ones obtained with conventional VGO, so he impact on the units balance would be negligible. Effect on the sulphur and diolefin content was not discussed. Torre et al[2] studied the effect of HZSM-5 addition to the catalyst on the product properties during the cracking of coker naphtha with vacuum gas oil. They reported that the presence of naphtha has an inhibiting effect on the cracking of gas oil, which was avoided by using sufficiently high catalyst/oil ratio (C/O>6). The presence of HZSM-5 zeolite in the catalyst causes a significant increase in the amount of LPG and decreases the aromacity of the gasoline.

Probably the most beneficial method of DCLN treatment is the catalytic HDS. However, hydrotreating of such a naphtha fraction is great challenge for several reasons. Firstly, olefin and diolefin content of coker naphtha fractions is very high. Formation of olefins is a result of high-temperature conversion reactions in the delayed coker. Upon contact with air, olefins and diolefins may form gum that complicates the transportation and processing of coker naphtha. Conjugated diolefins are of greatest concern. These unsaturated compounds act as precursors of gum formation and they promote coke formation reactions, especially at elevated temperatures. Therefore, proper control of exothermic olefin saturation is a key aspect of light coker naphtha hydrotreating. Prior to hydrodesulphurization, diolefins must be selectively hydrogenated to mono-olefins in order to stabilise the feed. Selective hydrogenation typically takes place in a separate reactor since very mild operating conditions are required, which are different from those of the HDS and HDN reactions. The saturation of diolefins is a very fast reaction and can therefore be carried out at high space velocities and at low temperatures. Conjugated diolefins polymerise at normal hydrotreating conditions, and the polymers cause fouling of the reactor resulting in pressure drop build-up. A generally accepted way of controlled saturation of conjugated olefins is to use a hydrotreating catalyst operated at low temperature (160-220°C) in the presence of hydrogen.

Secondly, degradation products of the silicone oil used as anti-foam additive in delayed coking is a threat to the catalysts of the downstream technologies. The silicone oil is a polydimethylsiloxane (PDMS). Because of gas formation, silicone oil is added to the coker drums to suppress foaming. Excess quantities of silicone oil will crack or decompose to form modified silica gels and fragments. These gels and fragments are mostly distilled in the naphtha range and are therefore carried to the downstream hydrotreaters together with the coker naphtha.

Breivik and Egebjerg[3] have recently conducted extensive studies to determine the mechanism of catalyst deactivation when subjected to coker naphtha feedstocks containing silicon. The found that PDMS decomposes at elevated temperature of the delayed coker, and they identified a homologue series of cyclic siloxanes in coker naphthas. Cyclo-siloxanes are quickly adsorbed on the catalyst surface. They showed that Si is present in the form of modified silica gels consisting partly of bulk SiO_2 with surface groups SiOH and $Si(OH)_2$ and partly of modified silica gels with methylated surface species. The deactivation is caused by adsorption on surface reaction sites reducing the amount of active sites that the sulphur and nitrogen species have access to. However, the loss of activity due to Si is irreversible and cannot be restored by catalyst regeneration. The deposition has been shown to be an activated and diffusionally controlled reaction catalysed by the surface alumina sites. This means that the silicon uptake capacity is higher for catalysts with higher specific surface areas and that, at higher bed average temperatures, the silica capacity of the catalyst will be higher. It was also found that the influence of Si deposition on catalyst activity is more pronounced for HDN than for HDS, thus HDN activity can be utilized to track the silicon contamination.

The third option to process coker naphtha fraction is its mixing into the feed of FCC gasoline desulphurization unit. Most of the refineries have already made investments to fulfil the future ultra-low-sulphur-gasoline specifications and built up plants for the desulphurization of FCC gasoline. Similar to coker naphtha, FCC gasoline has quite high olefin content (up to 30 vol.%). Hydrodesulphurization of FCC gasoline on conventional HDS catalyst results in significant loss of octane number due to the high degree of olefin saturation. Conventional hydrotreatment of FCC gasoline is therefore not cost-effective due to the octane loss and also the large hydrogen consumption needed for olefin hydrogenation. However, several well-proven commercial technologies (Prime-G+®, Scanfining, etc.) are already available on the market, which can provide deep HDS without significant loss of octane number. The heart of these technologies is the catalyst, which is able to suppress olefin hydrogenation while ensuring high HDS conversion at the same time. Detailed parameters of these technologies are reviewed elsewhere[4-6]. Selective FCC gasoline desulphurization processes are claimed to be suitable to process coker naphtha fractions, too. There are quite a number of studies[7-14] on the selective HDS of FCC gasoline itself but there much less or practically no information is available in the literature about the co-processing of coker naphtha with FCC gasoline.

2. Coker naphtha

The yield of coker naphtha is approximately 2.5% in reference to the feed of delayed coker unit. Expressed in capacity this means 25,000 MTPY. Table 2 compares the results of the test run compared with the corresponding design values. Sulphur content of the light naphtha fraction was considerably higher (0.47%) than the design value of 0.2%. Therefore the low quality DCLN fraction could not be directed into the gasoline blender otherwise the refinery could not have met the toughest gasoline specifications of the EU. Accordingly, desulphurization or other upgrading method was definitely required.

Table 2. Characteristics of the light naphtha fraction of Delayed Coker Unit

Characteristics	Design	Guarantee test run
Density, (15°C) kg/m^3	670	657
Sulphur content, %	0.19	0.47
Nitrogen content, mg/kg	18.0	66.5
Research octane number	82	88
Hydrocarbon composition		
paraffin	48	51
olefins	44	45
naphthenes, %	7	3.8
aromatics, %	1	0.2
Initial boiling point, °C	34	28
95% distilled, °C	max. 80	66
Final boiling point, °C	75	73
Silicon content, mg/kg	n.a.	5-10

Hydrocarbon composition of the DCNL is depicted in Figure 1. Olefins with a carbon number of 5-6 represent almost 37% of the naphtha, but the concentration of n-hexane, n-heptane is also significant. Roughly 4-5% of the olefins are diolefins, which is a remarkable concern for the refinery. Out of them butadienes and pentadienes are the most reactive ones, which have the biggest ability of gum formation in the gasoline.

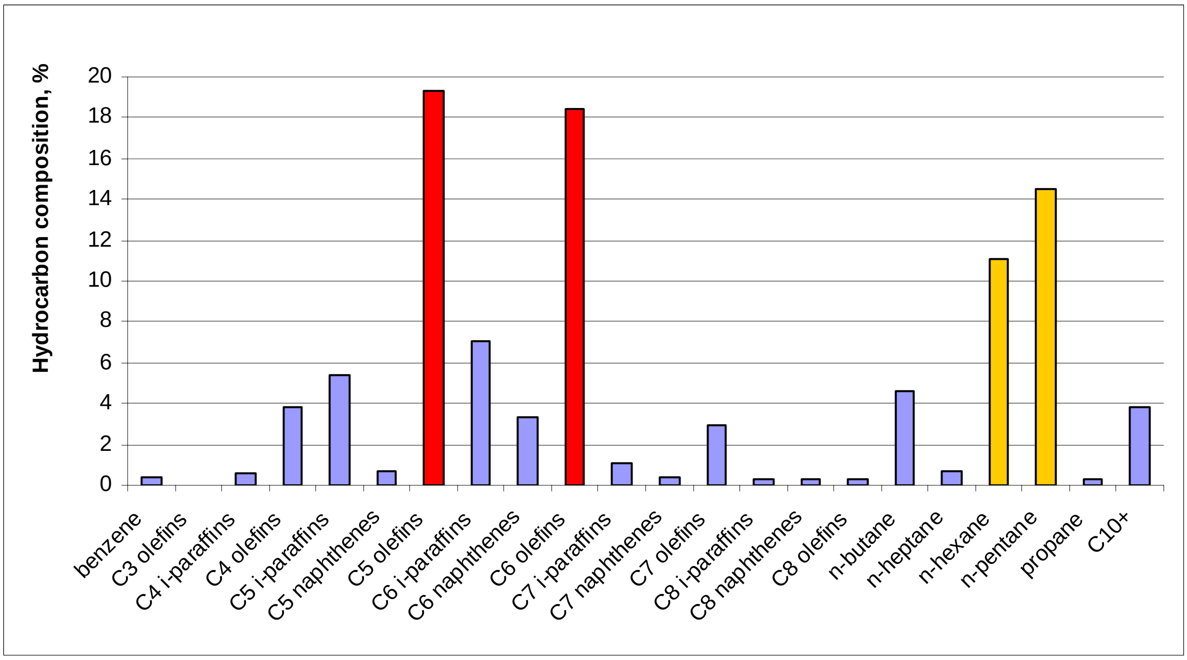

Figure 1. Composition of the delayed coker light naphtha fraction

Removal of the silicon content of the naphtha was also challenge for the refinery, since the deposition of silicone on the catalysts of downstream processing units may cause activity loss. Besides, engine gasoline has to be free of silicone, according the quality proposal of World-wide Fuel Charter as well to maintain the pollutant conversion activity of the emission control systems (three way catalysts) of the vehicles.

Due to the above-mentioned reasons the integration of the low-grade but high octane DCLN into the processing scheme of the refinery was a demanding task from the very beginning. After the start-up of the Delayed Coker Unit it was soon realized that the upgrading of DCLN is doubtfully necessary and evaluation of the possible treatment methods is required. Instantaneous test runs were needed to improve the quality of DCLN having much inferior parameters compared to the design values. Several opportunities were nominated, which were meant to manage the situation evolved:

- blending the DCLN into the feedstock of FCC Unit;

- processing of DCLN in the Atmospheric and Vacuum Distillation Unit;
- blending of DCLN into the feedstock of Gas Oil Hydrotreater;
- two-stage upgrading of DCLN in a suitable gasoline hydrotreater (selective diolefin saturation followed by HDS)
- blending of DCLN into steam cracker's feed (emergency option).

The processing of the coker naphtha was tested in four plants of the refinery: FCC Unit (riser), Atmospheric and Vacuum Distillation Unit (slop), Gas Oil Hydrotreater (HDS reactor) and Naphtha Hydrotreater Unit (HDS reactor) (Table 3.)

Table 3. Test runs for the integration of DCLN into the processing structure of the refinery

Period	FCC riser	A&V Distillation	Gas Oil HDT	Naphtha HDT
A	X			
B		X		
C	X			
D		X		
E	X			
F			X	
G				X

3. Processing of light coker naphtha in the FCC unit

Approximately 25,000 tones of coker naphtha was produced annually in the Delayed Coker Unit. Calculating with a diolefin content of 2.5% it corresponds to about 625 tones of diolefins annually, which is 0.05% of the feedstock of FCC unit. If the diolefins, which had been put into the FCCU feed with the DCLN, simply pass through the riser without conversion and they would be enriched in the gasoline fraction, their concentration would be nearly doubled, corresponding to about 0.1%. This would not be negligible compared with the general diolefin concentration effectively treated with anti-oxidant additives.

Theoretically, the diolefin content of the coker naphtha fraction would most probably be converted to coke and only small amount of them would remain unconverted and appear in the FCC gasoline. Although FCC catalysts are highly selective towards cracking and diene formation is minimized during catalyst development, it can not be totally excluded. Despite the very short residence time, some thermal cracking occurs beside the catalytic cracking reactions. Part of the dienes formed will act as a precursor of coke on the catalyst surface. The other part will appear in the FCC gasoline and may cause gum formation without prevention of it by additive treatment. Part of the diolefins routed to the FCC unit with the coker naphtha fraction reacts with the olefins present in the FCC gasoline (coke precursor); others from coke.

Calculations were performed about how the blending of DCLN into the feed of FCC unit would affect the sulphur content of the FCC gasoline. It was assumed that 10% of the sulphur in the FCC gasoline will appear in the FCC gasoline after fractionation. The worst scenario was considered when all the sulphur in the DCLN passes through the riser without any conversion, i.e. all of the DCLN's sulphur content will be present in the FCC gasoline. The calculated results are summarized in Table 4. According to these projections, significant increase in the sulphur content of FCC gasoline was possible in case of blending DCLN into the FCC feedstock.

Despite the expected and above-mentioned drawbacks, the light naphtha fraction had to be processed in the FCC unit after the start-up of the Delayed Coker Unit. DCLN was directed to the FCC unit in a varying volume in three different periods.

Figure 2 shows the share of DCLN in reference to the total FCC feedstock processed. The daily maximum percentage of DCLN never reached 2.5% of the total FCCU feed. Considering the operative standards of that time, sulphur content of the discharged FCC gasoline must not have exceeded 80 mg/kg, since in case of higher sulphur content the Gasoline Blending and Storage Plant could not have met the requirement of the standard (150 mg/kg).

Table 4. Sulphur balance of the FCC unit with/without DCLN processing

Features	**Units of measure**	**FCC gasoline products**			
		„A"	**„B"**	**„C"**	**„D"**
Feed of FCC unit					
Throughput	t/day	4000	3925	4000	3925
DCLN addition	t/ day	0	75	0	75
Total feed	t/ day	4000	4000	4000	4000
FCC gasoline product	t/ day	2160	2195	2160	2195
Sulphur in FCC feed	mg/kg	700	700	300	300
Sulphur in DCLN	mg/kg	-	2000	-	2000
Percent of FCC gasoline sulphur / FCC feed sulphur	%	10	10	10	10
Share of DCLN sulphur in FCC feed	%	0	100	0	100
Products of FCC unit					
Total sulphur input with FCC feed	t/ day	2.80	2.75	1.20	1.18
Sulphur input with DCLN	t/ day	0.00	0.15	0.00	0.15
Sulphur in FCC gasoline	t/ day	0.28	0.28	0.12	0.12
DCLN-derived sulphur in FCC gasoline	t/ day	0.00	0.15	0.00	0.15
Calculated sulphur in FCC gasoline	**mg/kg**	**130**	**194**	**55**	**122**

„A": no DCLN addition; end-of-run (EOR) conditions in the FCC feed pretreater
„B": 2% DCLN blended into FCC feedstock; EOR conditions in the FCC feed pretreater
„C": no DCLN addition; start-of-run (SOR) conditions in the FCC feed pretreater
„D" 2% DCLN blended into FCC feedstock; SOR conditions in the FCC feed pretreater

Figure 3 illustrates that the sulphur content of the FCC gasoline increased significantly, while the light coker naphtha was processed in the FCC unit.

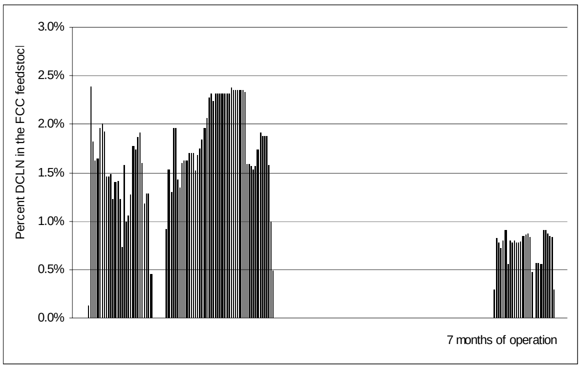

Figure 2. Daily volume of light coker naphtha in percentage of the total FCC feed

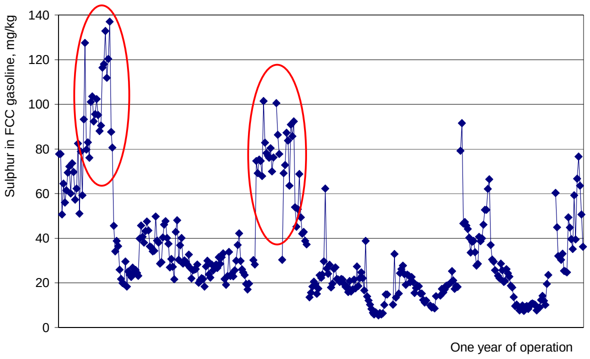

Figure 3. Sulphur content of the FCC gasoline

Sulphur content of the FCC gasoline was plotted in function of the sulphur content of the FCC feedstock. Figure 4 shows the correlation when the FCC unit was running with DCLN-containing feed while Figure 5 illustrates the case without DCLN addition. In the latter case, only the product of the FCC feed pretreater was processed in the FCC unit and the limit of 80 mg/kg sulphur was easily achieved. According to the expectations, there was a close correlation between the sulphur content of the feed of FCC unit and that of the produced FCC gasoline both with DCLN addition and without (R^2= 0.76 and R^2= 0,73, respectively). The dashed line represents the limit of highest sulphur content, which is still acceptable for the Gasoline Blending and Storage unit and results in trouble-free blending.

It was concluded that the processing of DCLN in the FCC unit caused serious quality problems of the FCC gasoline despite the fact that the percentage of DCLN in the total FCC feed never exceeded 2.5%. Since the DCLN is a very low-end fraction (final boiling point: max. 80°C) it is very difficult to crack. Subsequently, it tied up capacity of the FCC unit instead of producing a valuable product from it.

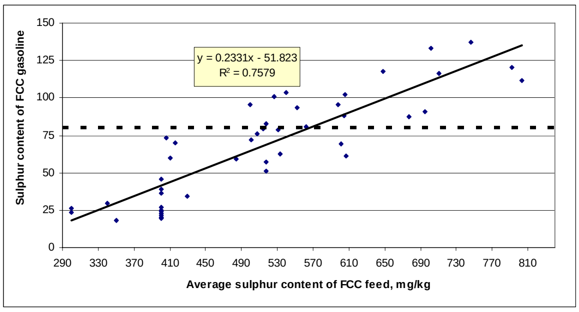

Figure 4. Correlation between the sulphur content of FCC gasoline and that of FCC feed (with DCLN co-processing)

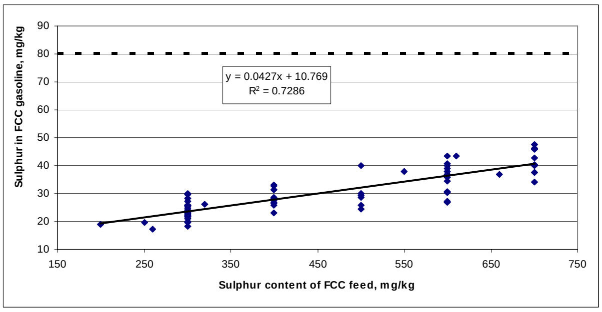

Figure 5. Correlation between the sulphur content of FCC gasoline and that of FCC feed (without DCLN co-processing)

4. Processing of delayed coker light naphtha in the AV Distillation Unit

In the next period of the coker naphtha was sent to a Atmospheric and Vacuum Distillation Unit. In these periods the coker naphtha was simply blended into the crude oil. The amount of coker naphtha was thought to be negligible compared with the streams of the AV units, and it was neither expected to cause major changes in the composition of crude oil nor in the function of the processing plants. Despite the enormous "dilution", the refinery had to face with the disadvantageous consequences of the mentioned action.

On the basis of the plant experiences, the light naphtha fraction of the Delayed Coker Unit increased the carbonyl sulphide (COS) content of the LPG product.

Carbonyl sulphide is present in the crude oil and also evolves during refining.
Upon heating COS decomposes:

$$COS = CO + S$$

or undergoes a transformation:

$$2\ COS = CS_2 + CO_2$$

or slowly hydrolyses in the presence of water

$$COS + H_2O = CO_2 + H_2S$$

All of the reactions produce gases, which deteriorate the quality of liquefied petroleum gas (LPG).

The other negative effect of blending of DCLN into the crude oil was the decrease the ability of lube base oil to release air, which was caused by the silicon content of the DCLN originating form the anti-foam additive applied in the coke drums of Delayed Coker Unit.

5. Processing of coker naphtha in the gas oil hydrotreater

The coker naphtha was not splitted into light and heavy fractions. Instead, the whole coker naphtha fraction was pumped into a Gas Oil Hydrotreater. The goal was to remove the sulphur content via hydrotreating in a plant, where the catalyst is not poisoned by the silicon content of the coker naphtha. Gas Oil Hydrotreater seemed to be the right choice. Approximately 4-5 cubic meters of light coker naphtha was sent to the plant hourly, which was hydrogenated without splitting prior to distillation. Unfortunately, this column was undersized for the actual throughput, i.e. serious separation problems occurred. In the absence of guard bed, fouling could have shown-up on the long-term caused by the gum-forming polymerization of diolefins.

Figure 6 shows the pressure drop of the gas oil stabilization column. Being aware of the plant status, the increased pressure drop of the column indicated the overloading the distillation tower as well as possible fouling problems.

In addition, pressure drop trend of the HDS reactor in the Gas Oil HDT plant clearly indicated an increase since the delayed coker naphtha fraction was processed in this plant (Figure 7). This was a clear indication of gum formation. Subsequently, the processing of coker naphtha resulted in difficulties in the gas oil hydrotreater plant as well, due to the risk of fouling and pressure drop increase. More rapid coking of the fired heater was a real risk even when heavy coker naphtha and light coker gas oil were processed. The light coker naphtha was an additional stream, which increased the silicon load of the hydrotreating catalyst, thereby decreasing its cycle length.

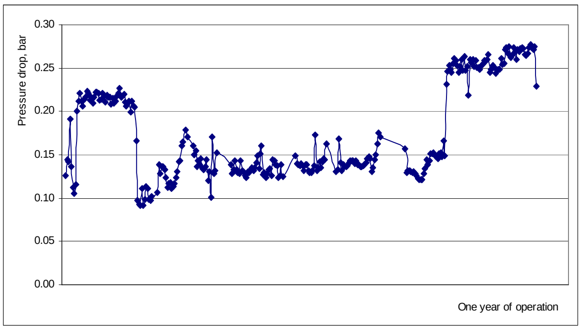

Figure 6. Pressure drop of the Gas Oil stabilization column

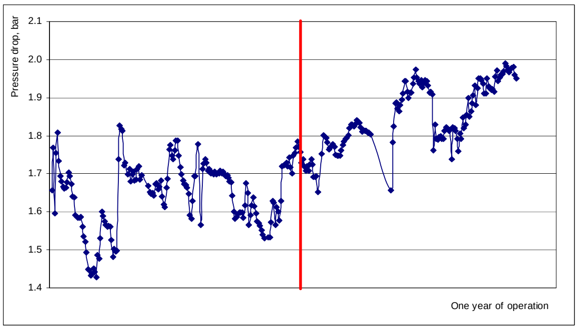

Figure 7. Pressure drop of HDS reactor in the Gas Oil Hydrotreater Unit

6. Two-stage hydrotreating of light coker naphtha

After all the preceding trials aiming the successful integration of the DCLN stream failed there was a pressure on the refinery to find a satisfactory solution for the upgrading of DCLN fraction. Laboratorial tests were carried out to evaluate the possibility of co-hydrotreating the DCLN with light virgin naphtha in two stages. The goal of the first stage was the selective saturation of the diolefins and to remove silicon impurities, while the task of the second stage was deep HDS and HDN with the objective of producing a valuable feedstock for the light naphtha isomerization unit. The results of the lab-scale test were more than encouraging, so the industrial realization was soon decided.

Considering the characteristics of the refinery, the Naphtha Hydrotreater seemed to be the most suitable plant for the HDS of DCLN. The plant was used for the hydrogenation of straight-run naphtha. Naphtha Reformer Unit, which had been previously shut-down, was selected for the selective diolefin saturation step.

In the first step of the process, the naphtha blend containing 10-20% of light coker naphtha and 80-90% virgin naphtha is passed through the first reactor, which was loaded with commercial NiMo/Al_2O_3 catalyst. Here the diolefins are selectively converted to mono-olefins and the deposition of the silicon-compounds takes place. The optimal temperature of the fist step was found to be 180-190°C. This temperature is high enough to adsorb virtually all of the silicon content of the naphtha but prevents gum formation and ensures high selectivity towards diolefin saturation at the same time. Hydrogenation of mono-olefins is negligible.

In the second reactor filled with a commercial CoMo/Al_2O_3 catalyst, deep HDS of the virtually diolefin- and silicon-free interim product takes place above 300°C. Sulphur and nitrogen content of the final product is less than 1 ppm.

The mentioned naphtha hydrotreater plants were revamped and prepared for the processing of the DCLN-LSRN blends. The test runs were conducted in July, 2003. Parameters of the test run are summarized in Table 5. Properties of the feedstocks and final product are given in Table 6. Table 7 compares the composition of diolefins and olefins in the feedstock, R1 effluent and R2 effluent.

The share of DCLN was successfully increased to 13% during the plant trials. As a result, the temperature of R1 (diolefin saturating reactor) effluent increased by 2°C and that of HDS reactor increased by 4°C. This was beneficial, since the energy surplus enabled the elevation of R1 inlet temperature. Removal of diolefins was virtually complete in the first step and the rate of HDS was satisfactory in the second reactor, while the olefin saturation was very high as well.

Table 5. Parameters of the test run for the two-stage hydrogenation of DCLN/LSRN blends (daily average)

Feature	**Period 1**	**Period 2**	**Period 3**	**Period 4**
LSRN, t/h (AV Unit)	33.1	33.1	33.0	34.4
DCLN, t/h	3.1	3.8	4.4	3.3
DCLN/LSRN, %	9.4	11.6	13.3	9.7
Feed of HDS reactor, m^3/h	54.8	55.7	56.6	57.1
Gas recycle, Nm^3/h	4691	4549	4514	4551
Final product, t/h	35.4	36.1	36.7	37.0
R1 pressure drop, bar	0.0	0.0	0.0	0.0
R2 pressure drop, bar	0.2	0.2	0.2	0.2
R2 inlet pressure, barg	20.5	20.5	20.5	20.5
R1 inlet temperature, °C	170	171	172	171
R1 outlet temperature, °C	170	171	172	171
R2 inlet temperature, °C	317	315	315	318
R2 outlet temperature, °C	337	338	341	339

Table 6. Main characteristics of DCLN/LSRN feedstock and final product (4 day average)

Characteristics	**Feed**	**Final product**
Density (15°C), g/cm^3	0.6741	0.6799
Sulphur content, mg/kg	864	0.2
Nitrogen content, mg/kg	6.6	0.6
Distillation, °C		
IBP	32.9	36
5%		43.1
10%	43.2	45.3
20%	47.4	48.6
30%	50.9	51.3
40%	54.9	54.9
50%	59.4	59.1
60%	64.9	64.3
70%	71.5	70.4
80%	78.8	77.3
90%	89.3	85.8
95%	97.1	91.6
FBP	105.5	94.4
Hydrocarbon composition, %		
n-paraffins	36.94	39.15
i-paraffins	34,38	36.65
olefins and diolefins	4.47	<0.1
naphthenes	22.37	22.34
aromatics	1.84	1.86

7. Conclusion

Sulphur content of the light coker naphtha fraction was 0.47%. Therefore the low quality DCLN fraction could not be directed into the gasoline blender. Instantaneous test runs were needed to improve the quality of the DCLN.

- by blending the DCLN into the feedstock of the FCC Unit the diolefins are converted in hydrogen transfer reactions, however, sulphur compounds pass through the riser without cracking that results in higher sulphur content of the FCC gasoline
- processing of DCLN in the "Atmospheric and Vacuum Distillation Unit" causes increased carbonyl sulphide level of the LPG product and abates the ability of the lube oil to release air
- although, the silicon content did not poison the HDS catalyst when the DCLN was processed in the "Gas Oil Desulphurization Unit", gum formation due to polymerization of diolefins appeared in the absence of guard bed and this resulted in pressure drop increase in the gas oil stabilization column and in the HDS reactor as well.
- two-stage hydrogenation of the DCLN blended into virgin naphtha was a satisfactory solution.

A valuable feedstock, which is virtually free of diolefins, silicon and sulphur can be produced for the light naphtha isomerization unit from the blend of coker naphtha and straight run naphtha with the two stage upgrading carried out over NiMo/Al_2O_3 and CoMo/Al_2O_3 catalysts, respectively.

Table 7. Comparison of the olefin and diolefin composition of the feedstock, interim product and final product of the two-stage hydrogenation

Olefins and diolefins	**Feed**	**R1 effluent**	**R2 effluent**	Olefins and diolefins	**Feed**	**R1 effluent**	**R2 effluent**
1-butene and i-butene	0.28	0.07	0.00	3-methyl-1-cyclopentene	0.06	0.02	-
trans-2-butene	0.08	0.06	0.00	3-methyl-2-cyclopentene	0.03	0.04	-
cis-2-butene	0.07	0.04	0.00	cis-2-hexene	0.05	0.12	-
3-methyl-1-butene	0.15	0.04	0.00	3,3-dimethyl-1-pentene	0.05	0.06	-
1-pentene	0.76	0.15	0.00	2,2,3-trimethyl-1-butene	0.01	0.00	-
2-methyl-1-butene	0.33	0.14	0.00	3,4-dimethyl-1-pentene	0.01	0.00	-
2-methyl-1,3-butadiene	**0.02**	**0.00**	0.00	1-methyl-cyclopentene	0.02	0.00	-
trans-2-pentene	0.29	0.39	0.00	2-ethyl-1-pentene	0.02	0.01	-
cis-2-pentene	0.15	0.18	0.00	3-methyl-1-hexene	0.02	0.02	-
2-methyl-2-butene	0.35	0.33	0.01	5-methyl-1-hexene	0.02	0.00	-
1-trans-3-pentadiene	**0.03**	**0.00**	-	4-methyl-1-hexene	0.04	0.01	-
1-cis-3-pentadiene	**0.02**	**0.00**	-	4-methyl-trans/cis-2-	0.02	0.02	-
cyclopentene	0.13	0.08	-	cyclohexene	0.04	0.03	-
4-methyl-1-pentene	0.14	0.04	-	3,4-dimethyl-cis-pentene	0.01	0.01	-
3-methyl-1-pentene	0.07	0.03	-	trans-3-hexene	0.04	0.05	-
2,3-dimethyl-1-butene	0.01	0.02	-	2-methyl-2-hexene	0.01	0.02	-
2-methyl-1,4-pentadiene	**0.01**	**0.00**	-	3-methyl-2-hexene	0.02	0.01	-
2-methyl-1-pentene	0.12	0.08	-	trans-2-heptene	0.00	0.05	-
1-hexene	0.51	0.07	-	3-ethyl-pentene	0.00	0.00	-
2-ethyl-1-buteme	0.01	0.00	-	cis-2-heptene	0.02	0.02	-
trans-3-hexene	0.03	0.06	-	2,3-dimethyl-pentene	0.02	0.03	-
cis-3-hexene	0.01	0.02	-	3-ethyl-cis-pentene	0.01	0.00	-
2-hexene	0.10	0.25	-	**Total unsaturated**	**4.47**	**2.98**	-
2-methyl-2-pentene	0.11	0.14	-				

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