Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 51 (2) 140-145, 2009

DEPENDENCE OF VISBREAKER RESIDUE PROPERTIES ON UNIT OPERATION SEVERITY AND THE RESIDUAL FUEL OIL SPECIFICATION

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Received November 27, 2008, accepted April 15, 2009

Abstract

A commercial test was carried out at the Lukoil Neftochim Bourgas, Bulgaria visbreaking unit. The visbreaker furnace outlet temperature was varied between 436 and 454^{0}C and the throughput was varied between 184 and 215 m^3/h. The increase of severity led to increase of 360^{o}C conversion from 18.7 to 25.1%. The visbreaker residue stability was found to depend not only on severity but also on the VGO content in the vacuum residue feed. The reduction of VGO content (increase of vacuum residue viscosity) allows achievement of higher conversion and production of stable visbreaker residue. The activation energy of the visbreaker process was determined to be 14.3 kcal/mol for the investigated conditions. The increase of conversion above 21% was associated with a reduction of visbreaker residue flash point in closed cup below 60^{o}C.

Key words: visbreaking; resid conversion; vistar stability.

1. Introduction

The visbreaking unit operation objective is to achieve maximum conversion of vacuum residue (diesel fraction maximum yield) and production of stable residual fuel oil. Typically, vacuum residue conversion is limited by the fuel oil stability. For this reason visbreaker units operate at maximum severity mode that ensures stable fuel oil production. In order to increase limit conversion over which visbreaker residue becomes unstable different additives may be used which allow achieving higher conversion without to vary fuel oil stability. However, visbreaker residue quality turns out that depends also on the fuel oil product specification. So, for example, if the specification includes norm for property flash point in open cup > 110^{o}C the severity is not restrictive for that property while at fuel oil specification including flash point in closed cup > 60^{o}C the severity is already limitation. With the purpose to optimize the vacuum residue visbreaking unit operation at the Lukoil Neftochim Bourgas, Bulgaria (LNB) and to achieve flash point in closed cup > 60^{o}C commercial test has been carried out. The aim of this work is to discuss results of the carried out commercial test.

2. Experimental

The present investigation has been carried out on the commercial vacuum residue visbreaking unit at LNB. Figure 1 depicts the simplified LNB visbreaker unit process scheme. The carried out test conditions has been as follow:

Throughput 215 m^3/h - Furnace outlet temperatures - 436, 442, 448, 454^{o}C
Throughput 190 m^3/h – Furnace outlet temperatures – 450^{o}C
Throughput 184 m^3/h - Furnace outlet temperatures – 445^{o}C

3. Results and Discussions

The visbreaker products distribution produced at different test conditions is presented in Table 1. The data show that the furnace outlet temperature increase from 436^{o}C up to 454^{o}C at throughput of 215 m^3/h results in conversion up to 360^{o}C increase from 18.7 % to 23.6 %.

Table 1 Visbreaking products distribution at different furnace outlet temperatures and different feed throughput

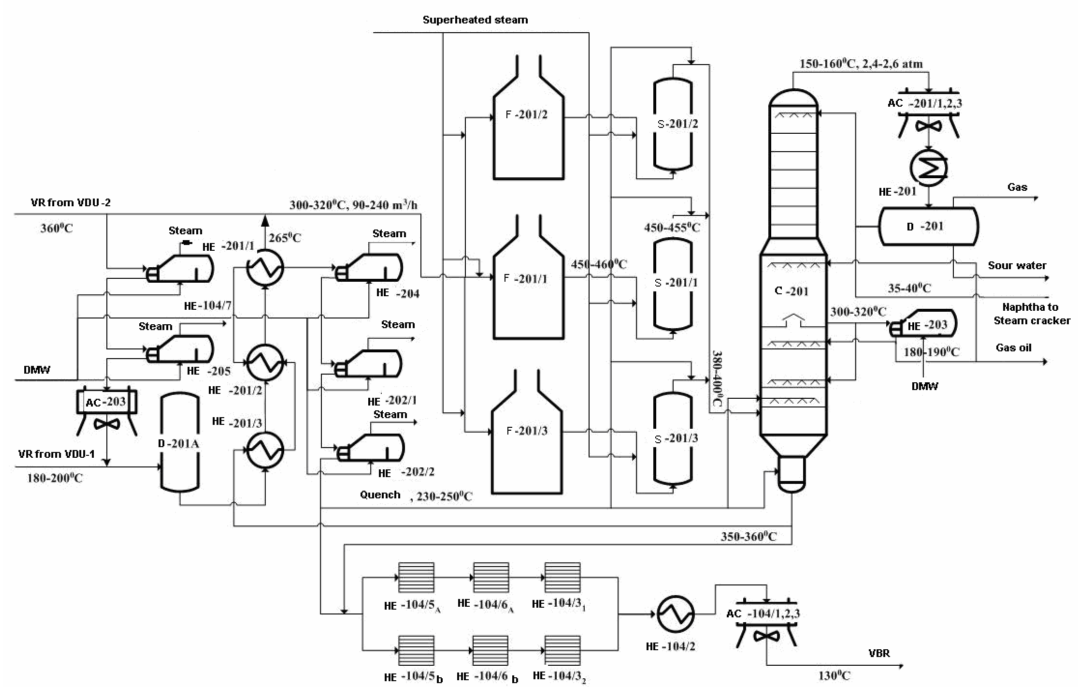
Throughput, m3/h	215		190		184	
Furnace outlet temperature, ^{o}C	436	442	448	454	450	445
Product distribution of the visbreaking unit, %						
Hydrocarbon gas	2.6	3.5	3.9	4.4	4.9	4.5
Gasoline	2.2	2.7	3.8	4.0	3.0	1.4
Diesel fraction	5.2	7.0	8.2	10.2	11.0	10.2
Visbreaker residue	89.9	86.8	84.1	81.4	81.2	83.9
Total	100.0	100.0	100.0	100.0	100.0	100.0
Vacuum residue conversion up to 360 0C, %	18.7	20.0	21.0	23.6	25.1	21.5

It is well known that vacuum residue visbreaking is described by first order kinetic equation of[2,3]. The kinetic constants for throughput of 215 m^3/h and the furnaces outlet temperatures in the range 436 – 454^{o}C are calculated using data from Table 1 and the acceptance that the furnace reaction volume + socking chambers is 120 m^3, and applying kinetic equation of first order (Ln(1-X) = k*1/LHSV). The graph of kinetic constant to temperature Arrhenius equation ($k=k_0.e^{-Ea/RT}$) is shown on Figure 2. The activated energy determined on the base of these data is Ea = 14.3 kcal/mol. This value is considerably lower than the value of Ea = 36 kcal/mol determined on the base of experiment carried out at temperature range 454 – 460^{o}C[1]. Two assumptions may be made by this comparison: 1) either feed properties has been different at the two tests or 2) the relationship of reaction rate to temperature is different for the two different ranges 436 – 454^{o}C and 460^{o}C. Table 2 summarizes vacuum residue properties and properties of visbreaker residue produced at its six operation modes of visbreaking.

Table 2 Vacuum residue, Visbreaker feed and residue properties at different operation mode

Throughput, m^3/h	215				194	184
Furnace otlet temperature, ^{0}C	436^{0}C	442^{0}C	448^{0}C	454^{0}C	450^{0}C	445^{0}C
Vacuum residue, Visbreaker feed properties						
Density, d_4^{20}	0.9969	0.9954	0.9891	0.9934	0.999	1.0007
Asphaltenes, %	3.3	2.2	3.5	3.1	2.6	3.7
Conradson carbon residue, %	15.1	16.0	17.2	17.9	16.0	17.2
ASTM D-1160 Distillation, ^{o}C						
IBP	408	390	369	360	363	337
5 % by volume	486	478	478	476	483	490
10 % by volume	500	506	508	512	505	500
14 % by volume						514
18 % by volume				524	518	
19 % by volume	505	512				
Relative viscosity at 100 ^{o}C, ^{o}E	75	65	63	82	85	90
Visbreaker residue properties						
Density, d_4^{20}	1.005	1.0007	1.0031	1.0007	1.0130	1.017
Relative viscosity at 100 ^{o}C, ^{o}E	58.0	46.0	40.0	43.0	57.0	55.0
Flash point in closed cup, ^{o}C	77	69	67	56	61	63
Asphaltenes, %	7.8	8.2	8.5	9.3	9.6	9.0
Conradson carbon residue, %	19.4	19.8	20.2	22.4	23.4	20.5
ASTM D-1160 Distillation, ^{o}C	% v/v	% v/v	% v/v	% v/v	% v/v	% v/v
350	8.5	6.8	5	7	6.8	7
360	9	7.5	6.5	8.7	8.5	8
400	13.8	12	11	14	14	12.8
440	19	18	18.5	21	21	19
480	26	26	28.5	30	30	28
510	32	32	38	38	39	34
540	38	40	46.2	46	48	42
Hot filtration sediments, %	0.018	0.033	>0.5	>0.5	>0.5	0.052
Hot filtration sediments after aging,	0.026	0.034				0.08

It is evident from these data that vacuum residue quality varies at different operation modes. The asphaltenes content varies between 2.2 % and 3.7 %; Conradson carbon residue is between 15.1 % and 17.9% and viscosity changes between 63 and 90°E. As refer to vacuum residue chemical nature it is difficult to conclude that it differs essentially since Conradson carbon residue, main characteristic property of residue petroleum fraction[4] varies in the range of test method precision (ASTM D – 189) and is within limits typical for vacuum residue, produced from crude oil type Russian Export Blend (REB). Hence, it may gathered that in present investigation Visbreaker feed chemical nature is typical for this vacuum residue, produced at REB crude oil distillation and is identical with that of Visbreaker feed used within the test carried in temperature range of 454 – 460°C [1]. Therefore, observe differences of the activating energy values may be due to the different temperature intervals at which the two tests are carried out.



Legend: C- Column; F – Furnace; D – Drum; S –Soaker; AC – Air Cooler: HE – Heat exchanger

Figure1. Scheme of the Lukoil Neftochim Bulgaria Visbreaker Unit

However, from the point of view of vacuum residue colloidal stability the vacuum residue quality varied considerably at different operation modes due to its different viscosity. As lower the viscosity the higher is the vacuum gas oil content in vacuum residue (Figure 3). It is well known that higher vacuum gas oil content is related with higher saturated hydrocarbon content in vacuum residue that advantage production of unstable residue at Visbreaker process [1]. This explains why at equal vacuum residue conversion observe at furnace outlet temperature 445°C and throughput of 184 m^3/h (feed relative viscosity of 90°E) and at furnace outlet temperature 448°C and throughput of 215 m^3/h (feed relative viscosity of 63°E) in first case it is produced stable Visbreaker residue (hot filtration sediment = 0.052 %) while at the second one hot filtration sediment content is over 0.5 %. Consequently, in order to produce stable Visbreaker residue it is required to maintain as higher as possible feed (vacuum residue) viscosity, respectively lower vacuum gas oil content in it. The data in Table 2 show that increase of operation mode severity at Visbreaker unit results not only to conversion increase but also to Visbreaker residue asphaltenes and Conradson carbon residue content increase. The conversion increase over 21 % results to the production of unstable Visbreaker residue (hot filtration sediments content is over 0.1 %). It is clear that value of that limit conversion may be increased by higher heavy vacuum gas oil recovery at atmospheric residue vacuum distillation and by adding of high aromatic FCC HCO (fluid catalytic cracking heavy cycle oil) and slurry from Fluid Catalytic Cracking unit to Visbreaker feed or by use of special additives (dispersants). The data in Table 2 show also that operation mode severity increase at Visbreaker unit results to Visbreaker residue flash point in closed cup decrease. Probably, that flash point decrease is due to main fractionator's pressure increase (Table 4). Hence, it may be concluded that Visbreaker unit operation mode severity is limited as of the produced Visbreaker residue stability so of it flash point in closed cup. It is established that conversion of 21 % is restriction as for Visbreaker residue stability so for achievement of the flash point in closed cup > 60°C specification for the investigated operational conditions interval at LNB Visbreaking unit.

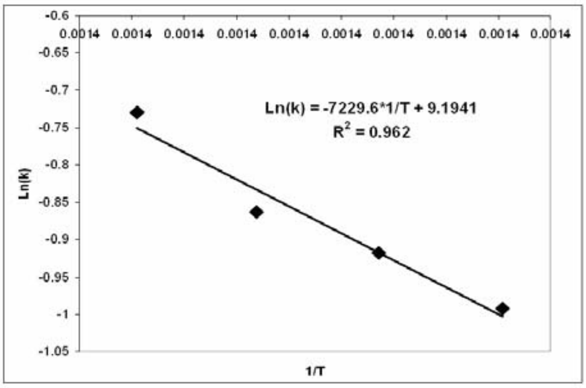


Figure 2 Arrhenius form plot for the temperature dependence of kinetic constant k

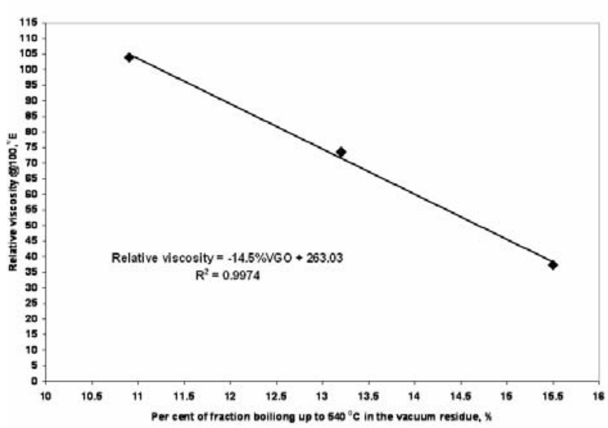


Figure 3 Relationship between vacuum residue relative viscosity and content of fraction distilled up to 540°C in it

Table 3 Diesel and gasoline physical- chemical properties at six operation modes

Throughput, m^3/h	215				190	184
Furnace outlet temperatures, °C	436°C	442°C	448°C	454°C	450°C	445°C
Gasoline						
Density, d_4^{20}	0.7246	0.7274	0.7353	0.7254	0.7204	0.7138
Distillation, ASTM D-86, % by volume	°C	°C	°C	°C	°C	°C
IBP, °C	34	35	37	42	31	30
5% v/v	59	58	60	63	54	54
10% v/v	68	70	70	73	65	63
20% v/v	84	86	87	90	79	76
30% v/v	96	98	98	103	90	87
40%v/v	106	108	109	112	100	96
50% v/v	115	118	118	122	108	104
60% v/v	124	127	126	130	117	111
70% v/v	131	136	133	139	124	114
80% v/v	139	143	143	148	134	126
90% v/v	150	156	161	164	145	138
95% v/v	210	-	-			
EBP, °C	270	180	182	238	178	178
Recovery, % v/v	96.5	97	97.5	97	96.0	96.0
FIA, % v/v						
Saturates	49.4	49.4	47.8	49.4		
Olefins	41.9	42.9	43.2	44.3		
Arenes	8.7	7.7	9.0	6.4		
Bromine number, g Br_2 / 100g	66.6	68.8	60.8	70.2		

Table 3 Diesel and gasoline physical- chemical properties at six operation modes, contd.

Throughput, m^3/h	215	190	184			
Furnace outlet temperatures, °C	436^0C	442^0C	448^0C	454^0C	450^0C	445^0C
Diesel						
Density, d_4^{20}	0.8374	0.8416	0.8466	0.8455	0.8393	0.8361
Distillation, ASTM D-86, % by volume	°C	°C	°C	°C	°C	°C
IBP, °C	157	150	160	162	157	142
5% v/v	190	189	192	189	175	181
10% v/v	197	202	206	200	190	188
20% v/v	213	216	220	217	208	202
30% v/v	225	229	233	230	221	216
40% v/v	238	241	248	246	239	232
50% v/v	253	258	264	264	258	249
60% v/v	270	277	283	281	277	269
70% v/v	287	297	302	302	290	280
80% v/v	306	317	325	326	320	311
90% v/v	330	342	355	354	358	341
95% v/v	350	369	375	372	380	362
EBP, °C	363	371	376	372	380	365
Recovery, % v/v	98.0	97.5	96.5	96.5	97.5	97.0
Bromine number, g Br_2 / 100g	33.3	32.0	32.6	31.4		

Table 4 Main fractionator's parameters

Furnace outlet temperatures, °C	436	442	448	454
Column top temperature, °C	135	147	144-150	147-150
Column bottom pressure, kg/cm^2	2.00	2.16	2.26	2.40
Column reflux vessel temperature, °C	46	46	46	44
URR (upper recycle reflux) flow, m^3/h	23.5	27	29	32
17th tray temperature, °C	192	200	208	208
MRR (mean recycle reflux), m^3/h	13.75	15.5	20.5	20
23th tray temperature, °C	296	312	324	330
Column bottom temperature, °C	376	378	378	378
Column bottom pressure, kg/cm^2	2.58	3	3.24	3.78
Quench temperature, °C	235	237	237	237
Quench flow, m^3/h	7-12	7-13	7-14	7-15
Column inlet temperature, °C	378	378	380	380
Product flow to the column, m^3/h	215	215	215	215

Table 5 Fuel oil quantity produced at the visbreaker unit different operation modes and additional quantity produced diesel fraction

Furnace outlet temperatures, °C	436	442	448	454
Visbreaker residue, t/h	146	141.0	136.6	132.1
FCC slurry, t/h	11.9	11.9	11.9	11.9
FCC HCO, t/h	9.7	9.7	9.7	9.7
VD diesel fraction, t/h	12.0	11.1	10.5	9.8
Fuel oil, t/h	179.8	173.7	168.6	163.6
VB diesel fraction, t/h	8.5	11.5	13.4	16.7
Delta diesel fraction, t/h*	-3.5	0.34	2.97	6.89

*Represents difference between the quantity of TC (visbreaking unit) and the VD (vacuum distillation) diesel fractions used as diluents for fuel oil.

Data of visbreaking unit gasoline and diesel fractions physical and chemical properties do not show any essential changes at unit operation mode severity variation. While in gasoline fraction it is noted light trend to olefin content increase (bromine number) in diesel fraction no change of bromine number was observed.

The present investigation results have been used to evaluate the change of fuel oil and diesel fuel quantity produced by the refinery in relation with vacuum residue conversion at TC (visbreaking) unit when fuel oil Visbreaker residue, FCC HCO and slurry from fluid catalytic cracking unit, and diesel fraction from atmospheric residue vacuum distillation unit are used as main components for their production at processing 7.1 million tones /year crude oil (Table 5). It is evident from the data in Table 4 that when operation mode severity increases, the quantity of the produced fuel oil decreases, while the quantity of produced diesel fuel increases. The quantity of the produced diesel fraction is lower than required to be added to commodity fuel oil in order to achieve viscosity specification requirement for residue fuel oil of 15°E at TC unit low operation severity. The requirement of adding straight run diesel fraction to commodity fuel oil drops out and even additional diesel fraction feed for motor diesel fuel (Euro diesel) production is obtained at TC unit higher operation severity. The economic analysis of these data at assumed prices for fuel oil, Euro diesel and low octane number gasoline 575, 1117 and 948 $ US/t correspondingly shows economic effect of the order of 15 millions $ US/year as the TC unit operation severity increases by 6°C.

4. Conclusions

The visbreaker unit furnace outlet temperatures (the operation severity) increase from 436°C up to 454°C results to increase conversion up to 360°C from 18.7 up to 23.6 %. The conversion increase over 21 % results to the production of unstable Visbreaker residue (hot filtration sediment content over 0.1 %) and flash point in closed cup lower than 60°C). This restrictive conversion may be increased via higher recovery of heavy vacuum gas oil at vacuum distillation unit, adding to TC unit feed of high aromatic fractions such as sludge and HGO from fluid catalytic cracking and use of special additives. The Visbreaker residue flash point in closed cup may be increased via main fractionator's pressure reduction. The economic effect achieved by operation mode severity increase of TC unit by 6°C amounts to about 15 millions $ US/ year.

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