

EFFECT OF PRESSURE ON DELAYED COKING OF ATHABASCA BITUMEN

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Introduction

Delayed coking, the most widely used coking process, was developed to minimize refinery yields of residual fuel oil by severe thermal cracking of feedstocks such as vacuum residue and thermal tars (Gary and Handwerk, 1984). The delayed coking process is particularly attractive when the green coke produced can be sold for anode or graphitic carbon manufacture or when there is no market for fuel oils, as in western Canada (Gray, 1994). The process uses long retention times in the liquid phases to convert the residue fraction of the feed to gases, distillates, and coke. The thermal cracking reactions produce olefinic species in the liquid product and the condensation reactions produce highly aromatic coke product that retains sulfur, nitrogen, and metals.

The effects of process conditions such as pressure, temperature, and residence time are important in determining the yield, selectivity, and quality of delayed coking products. Although plenty of information is available in the open literature regarding the effects of temperature and residence time on delayed coking products, very few data are presented on the effect of pressure. In the present work, we summarize the results of in-house pilot plant work carried out using Athabasca bitumen to study the effect of pressure on the yield and quality of delayed coking products.

Experimental

A schematic diagram of the delayed coker pilot plant is shown in Figure 1. The feedstock is loaded into a 200-L feed tank, which is typically heated to about 100°C to allow pumping of heavy oil/bitumen. The feed is then pumped through preheaters to the bottom of one of two coker drums. Typical feed rates range from 1 to 5 kg/h. Water supplied by a pulseless pumping system is fed into a heated coil and vaporized. The steam joins the oil at the entrance of the oil preheater, in which the steam and feedstock are heated further to the coker inlet temperature. The coker drum has a replaceable sleeve-liner, which is inserted to protect the inside of the coker drum and the end-cap seals. The liner also facilitates removal of the coke from the drum after the run. The sleeve is replaced after each run.

In the coker drum, the oil cracks into lighter liquids, noncondensable gases, and coke. The vapors, noncondensable gases, and steam leave the coker drum at the top and flow to a hot separator that is typically kept at 300°C. The liquid level in this vessel is controlled by adjusting the flow rate of the heavy ends (HE). HE are collected in a receiver maintained at atmospheric pressure. The remaining vapors/gases and steam are cooled and collected in a cold separator. From the cold separator, a light ends (LE) stream is removed that contains water and is collected in a receiver at atmospheric pressure. Uncondensed gases, together with solution gases from the light- and heavy-end receivers, flow through a pressure controller, which regulates the system pressure. They then pass through a dry test meter, and finally to a vent system. A slip stream of all gases, including process gas and dissolved gas, is sent to an on-line gas chromatograph for detailed compositional analysis. At the end of a run the feed is stopped

while steam continues to flow. After this steaming period, the drum heaters in use are turned off and the drum is cooled. After the drum and coke have been cooled the coke deposits are collected and stored.

Results and discussion

A full-range Athabasca bitumen was used as the feedstock in the delayed coker pilot plant. The chemical and physical properties are given in Table 1. All four runs were conducted under identical conditions except for the coker drum pressure, which was varied from 20 psig to 150 psig. The effects of coker drum pressure on the yields of total liquid product (TLP), gas, and coke are shown in Figure 2. Pressure increase suppresses vaporization in the coker drum and consequently increases the residence time of the liquid, thus allowing more cracking to occur. Due to the increased cracking, the yields of gas and coke increase and the yield of TLP decreases. The chemical and physical properties of TLP at different operating pressures are presented in Table 2. As the operating pressure increases, sulfur and nitrogen conversion increase as indicated by their reduced concentrations in the TLP.

The simulated distillation data with respect to different operating pressures indicate that the TLP becomes progressively lighter as the operating pressure increases. It must be noted that the yield of naphtha (IBP–177°C) fraction increases with increasing pressure similar to that of the light gas oil (177–260°C) fraction. The increases in the yields of the naphtha and light gas oil fractions were offset by the decrease in the yield of the residue fraction (316°C+). Chemical and physical properties of the naphtha, light gas oil, gas oil, and residue fractions obtained with respect to different operating pressures were analyzed. The coke properties, presented in Table 3, indicate that the concentration of sulfur and nitrogen decreases in the coke as the operating pressure increases, which is inline with the observation that the conversion of sulfur and nitrogen increases as the operating pressure increases.

Conclusions

Four delayed coking runs were completed successfully at different coker drum pressures while keeping other process conditions identical. The results from the experiments indicate that the yield of TLP decreases and the yields of coke and gases increase as the operating pressure increases. Sulfur and nitrogen conversions increase with increasing pressure.

Acknowledgements

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References

- Gary, J. H., Handwerk, G. E. *Petroleum Refining*, Second edition, Marcel Dekker, Inc. New York. 56, 1984.
- Gray, M. R. *Upgrading petroleum residues and heavy oils*, Marcel Dekker, Inc., New York. 244, 1994.

**Table 1 – Chemical and Physical Properties
Bitumen of Athabasca**

Analysis	Units	Value
Carbon	wt%	84.32
Hydrogen	wt%	10.43
Nitrogen	wt%	0.39
Aluminum	mg/kg	6.2
Barium	mg/kg	3
Calcium	mg/kg	26.1
Copper	mg/kg	1.9
Iron	mg/kg	13.4
Magnesium	mg/kg	1.6
Manganese	mg/kg	0.2
Molybdenum	mg/kg	9.6
Sodium	mg/kg	41.9
Nickel	mg/kg	80.3
Silicon	mg/kg	862
Titanium	mg/kg	2.4
Vanadium	mg/kg	218
Arsenic	mg/kg	0.2
Potassium	mg/kg	0.7
Sulfur	wt%	4.67
Density	g/mL	1.008
API gravity	API	8.88
ASH	wt%	0.04
Heptane insoluble	wt%	11.37
Hexane insoluble	wt%	11.2
Pentane insoluble	wt%	15.03
Toluene insoluble	wt%	0.01
Microcarbon residue	wt%	13.108
Molecular wt	g/gmol	525
Dynamic viscosity 60°C	cp	2810
Dynamic viscosity 100°C	cp	187

**Table 2 – Chemical and Physical Properties of TLP at Different
Operating Pressures**

Analysis	Units	20 psig	40 psig	150 psig
IBP–177°C	wt%	11.78	15.99	25.51
177–260°C	wt%	10.17	15.23	24.21
260–316°C	wt%	14.38	15.98	16.43
316°C+	wt%	63.66	52.80	33.84
Density at 15.6°C	g/mL	0.9149	0.9013	0.8716
API gravity	API	23.01	25.34	30.69
Carbon	wt%	84.84	85	85.08
Hydrogen	wt%	11.4	11.74	11.79
Nitrogen	mg/kg	1666.9	1502.75	1086.23
Sulfur	wt%	3.28	3.18	2.77
Ash	wt%	0.017	0.002	0.001
Pentane insolubles	wt%	0.058	0.05	0.054
Heptane insolubles	wt%	0.009	0.033	0.018
Hexane insolubles	wt%	0.041	0.014	0.03
Toluene insolubles	wt%	0.026	0.011	0.036
Microcarbon residue	wt%	0.751	0.5	0.457
Molecular wt	g/mol	395	427	466
Viscosity at 25°C	cSt	9.471	5.587	2.464
Viscosity at 40°C	cSt	5.993	3.9	1.874

Table 3 – Coke Properties at Different Operating Pressures

Analysis	Unit	20 psig	40 psig	150 psig
Density at 15.6°C	g/mL	1.389	1.383	1.347
Carbon	wt%	85.62	88.84	85.7
Hydrogen	wt%	3.97	3.75	5.67
Nitrogen	wt%	1.74	1.66	1.2
Sulfur	wt%	6.45	6.36	5.96
Pentane insolubles	wt%	99.464	99.769	80.743
Toluene insolubles	wt%	97.445	97.321	65.946
Calorific value	Btu/lb	14651	14915	14854
Aluminum	mg/kg	1.4	2.1	10.6
Calcium	mg/kg	21.5	35.8	50.8
Copper	mg/kg	1.8	20	103
Iron	mg/kg	19	66.5	242
Magnesium	mg/kg	1.4	2	3.7
Manganese	mg/kg	0.5	1.5	4
Molybdenum	mg/kg	15	35.2	23.5
Sodium	mg/kg	42.4	147	79.7
Nickel	mg/kg	214	352	283
Silicon	mg/kg	10.4	33.4	34.1
Titanium	mg/kg	4.2	7.7	5
Vanadium	mg/kg	575	926	672
Arsenic	mg/kg	<0.1	0.2	0.2
Mercury	ng/g	24	38	34
Moisture	wt%	0.21	0.3	2.66
Ash	wt%	1.72	0.43	7.67
Volatile matter	wt%	9.08	10.65	30.16

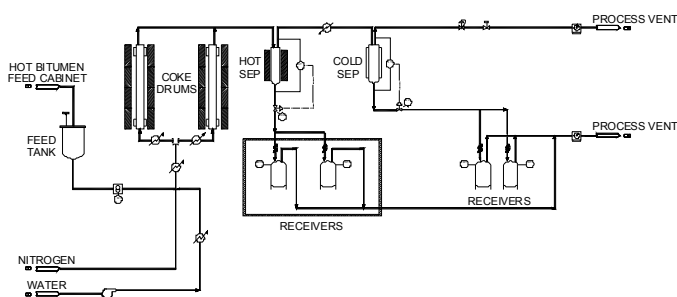


Figure 1 – Process flow diagram of delayed coker pilot plant

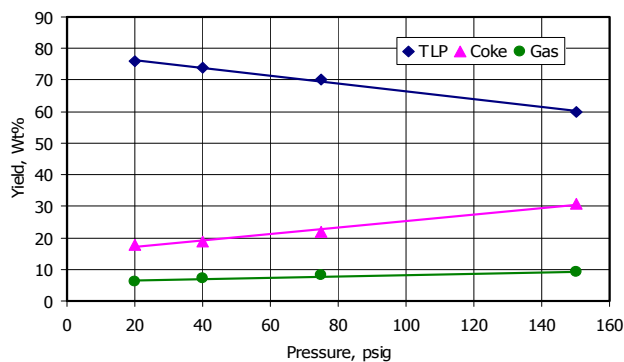


Figure 2 – Effect of pressure on TLP, coke, and gas yields