CORRELATION OF FEEDSTOCK PROPERTIES WITH COKING PROPENSITY UNDER HYDROPROCESSING CONDITIONS

By

J. F. Kriz
Energy Research Laboratories, CANMET, EMR Canada, 555 Booth St., Ottawa, Ont.
Canada K1A OG1

INTRODUCTION

Hydroprocessing is recognized as one of the primary upgrading steps in the conversion of heavy and residual oils to usable fuels. The chemical reactions which occur result in the reduction of the average molecular weight through cracking and hydrogenation. High yields of good quality liquid product can often be obtained, however, the consumption of high-pressure hydrogen has an important impact on economic considerations. Since the use of high-pressure hydrogen serves mainly in preventing the formation of coke, an assessment of feedstock coking propensity would be useful in the evaluation of the feedstock processability.

The coking propensity of a number of different feedstocks was experimentally evaluated and correlated with a selected set of their properties which were determined analytically. The wide range of relevant feedstock properties made it possible to establish their impact on the coking propensity.

EXPERIMENTAL

The feedstock coking propensity was assessed in a 155-mL tubular reactor having a length to diameter ratio of 12, three wire-wound heaters and a central thermocouple well. The feedstock was mixed with pure hydrogen at 10.4 MPa (1500 psig), 72 mL s^{-1} at STP and flowed continuously up through the reactor at an apparent liquid space velocity of 2 h^{-1}. One experimental run lasted 8.5h including startup and shutdown. The system was first pressurized with hydrogen and under hydrogen flow was heated to 300°C. Then, while maintaining conditions, the feedstock oil was pumped in for 1 h. Subsequently, the temperature was elevated to a pre-determined level in about 0.5 h by supplying constant power to the reactor heaters. The temperature level was maintained for a period of 5 h during which changes in reactor temperature profiles were observed and two liquid product samples were collected. At shutdown, the heaters were turned off, and when cooled to 390°C the reactor was isolated from the flow system and its fluid content was drained by using the pressure of the residual gas. Thereafter, the entire solid residue in the reactor was carefully collected.

ANALYTICAL INFORMATION

Feedstocks were analyzed to determine relative density, 16/16°C (DENS), and wt per cent of Conradson carbon residue (CCR), pentane insolubles (PI), ash-free toluene insolubles (TI), a fraction boiling above 524°C or 975°F (PITCH), carbon, hydrogen, nitrogen (N), sulfur(S) and ash (ASH). Hydrogen and carbon analyses were used in terms of hydrogen to carbon atomic ratios (H/C). Analytical data are shown in Table I. Liquid samples collected during experimental runs were analyzed for weight and relative density to examine the material balance and to obtain further evidence of the extent of coking. However, this information was not used in the interpretation of results. Five of the feedstocks tested were heavy crude oils from Canada and Venezuela. A heavy gas oil fraction of one of these was included separately. Residual oils were refinery blends of

various origins, five of which were vacuum tower bottoms.

TABLE I

FEEDSTOCK PROPERTIES AND FEEDSTOCK PROPENSITY DATA

Feedstock	CCR	PITCH	DENS	PI	TI	H/C	N	S	ASH	T_F	T_{FC}
Heavy Gas Oil	0.0	0.0	0.992	0.0	0.0	1.475	0.38	3.6	0.00	480	480
Resid 1	15.9	90.0	0.989	11.8	1.74	1.558	0.45	1.33	0.034	458	456
Heavy Oil 1	13.3	51.0	1.009	15.5	0.72	1.452	0.4	4.5	0.59	457	460
Resid 2	14.0	15.0	1.064	27.6	0.06	1.074	0.05	0.2	0.00	457	456
Resid 3	10.6	54.5	0.975	7.3	0.04	1.518	0.46	3.01	0.02	453	453
Heavy Oil 2	15.8	67.0	1.024	19.1	0.28	1.451	0.4	5.2	0.08	451	450
Resid 4	17.4	99.4	1.009	15.8	0.14	1.339	0.74	1.8	0.026	448	446
Heavy Oil 3	16.7	67.0	1.016	22.3	0.09	1.497	0.8	5.7	0.24	447	447
Heavy Oil 4	18.2	73.0	1.026	21.0	0.03	1.479	0.6	5.2	0.06	447	445
Heavy Oil 5	19.0	82.0	1.023	18.6	0.26	1.434	0.5	3.3	0.12	445	447
Resid 5	18.6	95.1	1.022	21.5	0.1	1.308	0.72	3.34	0.12	443	445
Resid 6	23.0	80.0	1.025	20.0	0.12	1.386	0.4	0.0	0.02	443	443
Resid 7	22.3	98.3	1.019	15.9	0.01	1.43	0.3	4.3	0.03	442	442
Resid 8	25.6	99.0	1.031	20.1	0.15	1.415	0.4	4.5	0.05	440	440
Minimum values	0.0	0.0	0.950	0.0	0.0	1.000	0.0	0.0	0.0	420	
Maximum values	30.0	100.0	1.100	40.0	3.0	1.600	1.0	7.0	1.0	490	
a_i and A*	-0.48	-0.06	0.29	-0.23	0.20	0.01	-0.01	-0.04	0.10	1.75*	

Data Treatment

The experimental method described earlier provides information which is used for determining temperature T_F associated with a certain amount of reactor residue (coke) formed during the run. This can be accomplished graphically as shown in Figure 1. Values of selected feedstock properties can then be correlated with the T_Fs of individual feedstocks. Although the correlation can be performed by various empirical approaches, the present one evaluated the constant A and powers a_i in the empirical formula

$$Y = A \prod_{i=1}^{k} X_i^{a_i} \qquad \text{1)}$$

where X_i relates to k selected feedstock properties and Y relates to T_F. The values in Table I were transferred to the pertinent X_i and Y by "scaling" which uses chosen minimum and maximum quantities in the relationship

$$X = 1 + \frac{p - p_{min}}{p_{max} - p_{min}} \qquad \text{2)}$$

where X is the scaled quantity and p is either property or T_F values in Table I. It appears from Equation 2 that all the scaled variables X_i and Y assume values between 1 and 2 while exhibiting comparable deviations within these limits. The limiting values p_{min} and p_{max} were chosen to suit the expectations and are also shown in Table I. The scaling seems appropriate with respect to the use of Equation 1 because the powers a_i indicate the effect of the property on coking propensity which is independent of the dimension and magnitude of the property measure.

The parameters a_i and A in Equation 1 were evaluated statistically by applying multiple least squares regression and using different combinations of feedstocks and their properties. This procedure helped to establish the correspondence between changes of a property value and T_F rather than the best numerical fit.

RESULTS AND DISCUSSION

Values of T_F (°C), associated with the feedstock coking propensity, corresponded to the information of 53 g of reactor residue and are included in Table I. As shown in Figure 1, the amount formed increases with increasing T, thus feedstock coking propensity must be higher for lower values of T_F. As expected the highest T_F (480°C) was obtained for the heavy gas oil having less tendency to coke. T_F values for the rest of the feedstocks varied between 440 and 458°C and

are shown in decreasing order (increasing coking propensity) in Table I.

The results of the parameter evaluation are given at the bottom of Table I and show the a_i quantities for each feedstock property. For the set of parameters shown, a five-variable analysis indicated a multiple correlation coefficient of 0.988 for the 14 feedstocks. Applying the set of parameters to Equations 1 and 2, the back-compound values T_{FC} at the right-hand side of Table I can be compared with the T_F values. The differences are within 3°C, which is considered to be the extent of experimental error in determining T_F.

The magnitudes and signs of the a_i quantities can be used to assess the effects of properties on coking propensity. Thus high values of CCR and PI indicate severe coking propensity while high values of density, TI and ash content tend to reduce it. The comparative effects of H/C, nitrogen, sulfur and pitch content are marginal. Unfortunately, most of the property variations cannot be rationalized as independent; some are actually quite interdependent. Obviously, feedstocks having higher contents of CCR and PI would likely be "heavier" in terms of their density, and thus in the empirical relationship the positive effect of density would somewhat offset the negative effects of CCR and PI. However, the combined effect of the three may be interpreted in terms of general reactivity, since among the large molecules the high density ones are probably more stable than the less dense molecules. Further, it appears that the presence of inert solids of carbonaceous or mineral nature, as identified by TI and ash components, would provide additional lowering of coking propensity.

Coke formation under hydroprocessing conditions occurs as cracked intermediates are re-constituted into large polymers. This phenomenon can be observed microscopically with the appearance of anisotropic mesophase spheres which grow through coalescence and ultimately form coke. Different types of coke have been found to form in the reactor depending on the feed component(1). Obviously, a variety of molecular types can take part in coke formation although the large molecules, which are present in heavy and residual oils but absent in gas oils, are more likely to form mesophase.

It would be beneficial to link the coking propensity to compound-type characterizations as this would allow evaluation of the coke formation as a competing reaction. However, this approach is uncertain when analyzing large molecules. For example, discrepancies in determining average molecular weight of bitumen have been explained only after a detailed examination of solvent effects on such oils (2).

When hydroprocessing is applied as the primary upgrading step, the key role of hydrogen is to prevent coke formation. This requires effective hydrogen transfer to the unstable species so that the chain of events involving molecular growth or coalescence is interrupted by saturation. Typically, the maximum conversion of pitch depends on the maximum operating temperature that can be applied without causing reactor coke formation. The higher the feedstock coking propensity, the more effective hydrogen transfer is needed to achieve comparable conversions, which can be established by further increasing the hydrogen pressure or using hydrogenation catalysts. Another alternative is using solid additives (3) which lower the coking propensity when slurried with the feedstock. Actually, the main function of effective additives is to enhance the hydrogen transfer and is exhibited in the lowering of coking propensity (4). An additional function is that of an inert solid, as shown earlier, which possibly interferes physically with the coalescence and growth of mesophase. The extent of the lowering of coking propensity by solid additives was found to depend on both the additive and feedstock properties. A modified set of parameters would have to be established to assess processability for each functional additive.

SUMMARY

–An experimental method is described whereby the feedstock coking propensity under hydro-processing conditions is assessed.

–Temperature values associated with coking propensities of 14 feedstocks are shown.

–These are correlated with a selected set of feedstock properties using an empirical rela-tionship.

–Parameters obtained are used to indicate the impact of changes in feedstock properties on processability.
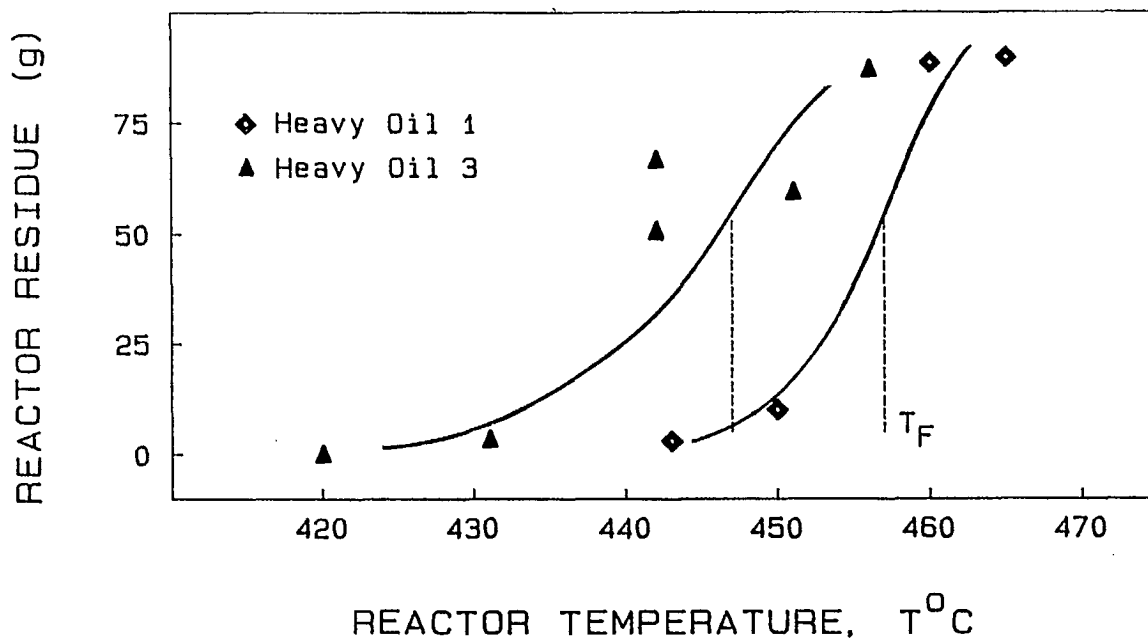
ACKNOWLEDGMENT

Fig.1: Amount of residue vs. operating temperature for two feedstocks. Coking propensities indicated by T_F

LITERATURE CITED

(1)   Nandi, B.N., Belinko, K., Ciavaglial,L.A.and Pruden, B.B., Fuel, 57 265-8 (1978).
(2)   Champagne, P.J., Manolakis, E. and Ternan, M., Fuel, 64, 423-425 (1984).
(3)   Kriz, J.F., Ternan, M. and Denis, J.M., J.Can.Pet.Technol. ,22, 29-34(1983).
(4)   Kriz, J.F. and Ternan, M., "Hydrocracking heavy hydrocarbon feedstocks: Aspects of catalysts related to feedstock coking tendency" in Studies in Surface Science and Catalysis, Vol. 19: Catalysis on the Energy Scene, S. Kaliaguine and A Mahay (Editors), Elsevier Publishing Co., Amsterdam, pp. 545-52 (1984).