

Reducing Viscosity of Coal Liquefaction Products With Additives

T. S. Chao, H. W. Kutta and A. C. Smith, Jr.

ARCO Petroleum Products Company
Harvey Technical Center
Harvey, IL 60426

Introduction

Viscosity is one of the critical properties hindering the development of coal liquefaction processes. A product of high viscosity is difficult to pump, filter and atomize, affecting the flow of process streams, removal of catalysts, transport from one location to another and proper atomization in combustion equipment. The use of higher temperatures to reduce viscosity is costly and is often accompanied by problems of oxidative and thermal degradation and safety.

Viscosity can be reduced by more extensive hydrogenation. This practice, however, increases the cost of product and may not be necessary. If the cause of high viscosity of coal liquefaction products is thoroughly understood, an economically attractive alternative to extensive hydrogenation can probably be found. A research program to investigate the cause of high viscosity of coal liquefaction products and to improve this critical property was carried out at Harvey Technical Center under the joint sponsorship by Electric Power Research Institute and Atlantic Richfield Company. Results of this program have been issued as an EPRI report.(1) Prior to this joint program an in-house project was also initiated by Atlantic Richfield to determine causes and remedies for high viscosity of coal liquefaction products. One result of these programs is the discovery that certain chemical compounds, when used at concentrations of 1-10%, are effective in reducing the melt viscosity and softening temperature of these coal liquefaction products. This paper summarizes our findings on this subject and expresses our thinking regarding their mechanism of action.

Experimental

Source of Coal Liquefaction Products

1. H-Coal

H-Coal was provided by Hydrocarbon Research, Inc., Trenton, NJ, and was identified as PDU Run 130-73. This pilot plant run was operated at a fuel oil mode meaning that less extensive hydrogenation was carried out. This yielded three fractions: atmospheric overhead, atmospheric bottoms and vacuum bottoms. The last-named fraction contained catalysts and other ash-forming materials. It was de-ashed in our laboratory by dissolving in tetrahydrofuran, filtering through a fine-pore filter aid (Celatom FP-2 from Eagle-Picher Industries) and removing the solvent by diluting with water, filtering, washing and drying in a vacuum oven. The de-ashed vac. bottoms was then combined with the other two fractions according to the proportions

provided by Hydrocarbon Research. To avoid oxidation all operations were carried out under N_2 atmosphere and all materials were stored in desiccators or closed containers under N_2 . Analyses of the different batches of H-Coal used for this study are shown in Table 1.

2. SRC-Coal

Solvent Refined Coal was provided by Catalytic, Inc., Wilsonville, AL. It was produced from Illinois No. 6 Coal of Burning Star Mines and was used as received in our studies. Analyses are also shown in Table 1.

Source of Additives

All the additives discussed in this paper (except naphthenic acid and aromatic oils) were purchased. Suppliers and chemical structure are shown in Table 6.

Blending

In the case of H-Coal the components were weighed into a N_2 -flushed screw-capped Pyrex jar, heated in an oven at $350-360^{\circ}F$ until the solids melted and were then stirred under a N_2 blanket into a homogeneous mixture. The jar was closed, cooled to room temperature and the solid mass was pulverized into a powder under N_2 blanket. This powder was used for analysis, for melting point and softening point determinations and for blending with additives. H-Coal and less volatile additives were weighed directly into the Brookfield viscometer cup. This procedure avoided oxidation of the product during hot blending and was more convenient than carrying out the blending in an autoclave. However, it also limited the quantity of H-Coal blended in each batch and a total of six batches had to be prepared for this study. An autoclave was used when more volatile additives, e.g. propylene oxide, acetic anhydride and acetic acid were employed.

For Solvent Refined Coal the same procedure was followed except that no blending from components was required.

Viscosity Determination

Viscosity was determined in a Brookfield Viscometer (Model RVT) at temperatures of $278-500^{\circ}F$ and shear rates of 14 and 28 sec^{-1} . These correspond to speeds of 50 and 100 rpm with the SC 4-28 spindle. All viscosity data were based on an average of three readings which were usually within 2% of each other. Temperatures shown for the viscosity data were actual temperatures based on calibration. Low and inconsistent viscosity readings obtained for non-homogeneous samples were disregarded.

Softening Point Determination

The softening point was determined according to ASTM Method D-2398. To avoid excessive oxidation, the preparation of the sample disc was carried out under N₂ atmosphere in the laboratory of one of the investigators.

Results and Discussion

The additives found to be effective at 1-10% level can be divided into two groups: those which are reactive with certain components of coal liquefaction products and those which are unreactive. These materials are defined as additives on the basis that they perform an essential function at a relatively low concentration.

Reactive Additives

The presence of acidic and basic components in coal liquefaction products is well known. Sternberg and his coworkers⁽²⁾⁽³⁾⁽⁴⁾ reported that asphaltenes, the key intermediate of coal liquefaction, contains both acidic and basic components and that the hydrogen bonding between these components is responsible for the high viscosity of the products. The acidic components include phenols and pyrroles, while the basic components are pyridines.

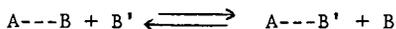
Based on this knowledge we postulated that any chemical compound which can react with either the acidic or basic groups will reduce the viscosity of coal liquefaction products by converting the acid or basic components into neutral ones and, in so doing, eliminate the strong intermolecular forces causing high viscosity. The postulation was proved to be correct. Fig. 1 shows the viscosity of a H-Coal with and without the presence of 5% by weight of various reactive additives. Table 2 shows the effect of these additives on softening temperature and a calculated % reduction of 330°F viscosity. These additives represent the following class of chemical compounds. Only one or two compounds in each class were tested and consequently, may not represent the optimum choice. The latter is dependent on cost, availability, effectiveness and such considerations as volatility, corrosiveness, toxicity, safety and ease of handling.

a. Acids and Anhydrides

These compounds are expected to convert the basic nitrogen compounds to salts or amides, eliminating the H-bonding with the weaker phenolic compounds. Compounds tested include naphthenic acid, acetic acid, acetic anhydride and dodecenylic succinic anhydride. At a concentration of 5% W, the reduction in 330°F melt viscosity was 82-89%. In later work with 1 and 2% acetic anhydride and a different batch of H-Coal reductions of 355°F viscosity of 40.5 and 52.5% were obtained. (Table 4)

b. Amines

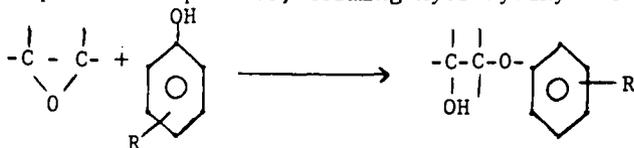
The amines selected for testing were Cocoamine and Duomeen C, based on considerations of volatility. At 5% W they reduced 330°F viscosity of H-Coal by 72.6-81.0%. These amines (represented by B') probably function by replacing the weaker pyridine type components (B) from the hydrogen bonding pair A---B.



The new hydrogen bonding pair formed A-B' will have lower viscosity, since B' is a smaller molecule than B.

c. Epoxides

Epoxides can react with the phenolic compounds in the coal liquefaction product, forming hydroxyalkyl ethers.



The epoxides tested included propylene oxide and Epoxide No. 7, a glycidyl ether of a mixture of n-C₈ and n-C₁₀ alcohols. The former lowered 355°F viscosity of one batch of H-Coal by 56.7% when used at 2% W. The latter lowered the 330°F viscosity of another batch by 84.3%, when used at 5% W. The effect of concentration of propylene oxide on viscosity of H-Coal is shown in Table 4.

Unreactive Additives

Compounds of this type are not expected to react chemically with components of coal liquefaction products. Table 3 shows their effect on viscosity and softening point of H-Coal. At a concentration of 5% W they reduced the 330°F melt viscosity of H-Coal by 76.3-95.5% and lowered the softening point by 17-81°F.

One most promising compound is N-methyl-2-pyrrolidone (NMP). At 5% W it gave the largest reduction in viscosity, 95.5%, among the compounds tested and is shown in Table 4. Subsequent concentration studies indicated that it is quite effective even at 1% W. The results of this concentration study are shown in Table 4 and illustrate that 68.0-78.4% reductions of the 330°F viscosity was achieved with 1% N-methyl-2-pyrrolidone for different batches of H-Coal. Fig. 2 shows viscosity of H-Coal as a function of temperature and concentration of NMP.

These compounds belong to the chemical classes of amides, phosphoramides, lactams and ketone. They are all polar compounds with moderate hydrogen bonding characteristics. Their ability to reduce the viscosity of H-Coal is believed to be related to their strong solvent power for the asphaltenes and preasphaltenes. Altgelt and Harle⁽⁵⁾ reported that viscosity of solutions of petroleum asphaltene is dependent on the nature of solvent. A good solvent such as pyridine provides a much lower solution viscosity for a petroleum asphaltene than a poor solvent such as cyclohexane. From this and related observations they concluded that viscosity of asphalts depends considerably on the intermolecular aggregation of dissolved asphaltene and the extent of aggregation is dependent on the solvent.

The situation encountered with H-Coal is believed to be similar in the sense that good solvents did reduce viscosity and that the high viscosity is caused by aggregation. Differences may exist in the cause of aggregation. Altgelt and Harle, referring to studies by Yen et al⁽⁶⁾, described the aggregate as the stacking of condensed aromatic rings. For coal liquefaction products, the work of Sternberg also indicated that aggregation of asphaltene molecules is caused by intermolecular H-bonding between acidic and basic groups. Regardless of the exact mechanism we can expect that aggregation of molecules does exist in coal liquefaction products and that good solvents can alter the extent of aggregation and thereby reduce its viscosity.

One important difference between the present case and that of Altgelt and Harle is the relative proportion of solvent and solute molecules. In the latter case the highest concentration of solute was 26.8% and the predominant species in the solution is that of the solvent. In the case with H-Coal and 1% NMP it is estimated that each molecule of NMP has to exert its effect on 10-15 molecules of asphaltene or preasphaltenes. This seems to indicate that these asphaltenes and preasphaltene molecules do exist in aggregates of 10-15 and more and that NMP exerts its effect not on individual molecules but on these aggregates.

Effectiveness in Solvent Refined Coal (SRC)

a. Reactive Additives

SRC from Illinois No. 6 coal was treated with 1 and 2% of propylene oxide, acetic acid and acetic anhydride in an autoclave. A reaction temperature of 500°F was maintained for 30 min. The treated product had a viscosity 15-40% lower than the original SRC (Table 5). This improvement was considerably less than that occurred with H-Coal (40.5-56.7%) under comparable test conditions.

b. Unreactive Additives

Of the many unreactive additives found effective in H-Coal only one was chosen for treatment of SRC. Results indicated that N-methyl-2-pyrrolidone gave a 48.2% reduction of 430°F viscosity at a concn. of 4% W.

However, a number of aromatic petroleum by-products were found to be effective at concentrations of 10%. Data in Table 5 show that the two aromatic extracts reduced the 440°F viscosity by 44.0-72.5%. These are by-products from solvent refining of 200 and 100 viscosity (SUS @ 100°F) lubricant base oils. The concentration of aromatic hydrocarbons by clay-gel analysis is in the range of 66-70%. The two light cycle oils reduced the 440°F viscosity by 78.0-83.5%. They are by-products of fluid catalytic cracker and contain approximately 60% aromatic hydrocarbons. The effectiveness of these additives is apparently related to the presence of high concentrations of aromatic hydrocarbons and their better solubility for the components of SRC. The greater effectiveness of light cycle oils than the aromatic extracts is believed to be related to their much lower viscosity.

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Table 1
Composition of Coal Liquefaction Products

Identity Batch No. ^a Analyses	H-Coal				SRC
	1	2	3	6	1
Wt. % C	85.65	85.65	86.75	85.34	86.90
H	6.71	7.15	7.30	7.38	5.75
O	4.66	4.11	4.12	4.80	5.00
S	0.70	0.62	0.57	-	0.67
N	1.39	1.28	1.27	1.28	2.00
Ash	0.14	0.17	0.21	0.15	0.24
H ₂ O	0.32	1.86	0.13	-	-
Mol. Ratio H/C	0.93	0.99	1.00	1.03	0.79

^a Batches 4 and 5 were blended with same proportions of atmospheric overhead, atmospheric bottom and de-ashed vac. bottoms as Batch 3. They were not analyzed.

Table 2
Effect of Additives on Viscosity and Softening Point of H-Coal^a

Additive	Wt. %	Softening Point °F		% Reduction Viscosity at 330°F
		<u>Determined</u>	<u>Reduction</u>	
None	-	275	-	-
Naphthenic Acid	5	210	65	82.1
Acetic Anhydride	5	235	40	88.8
Dodecenyl Succinic Anhydride	5	223	52	84.4
Cocoamine	5	200	75	81.0
Duomeen C	5	210	65	72.6
Epoxide No. 7	5	203	72	84.3

^a Batch 2, Brookfield Viscosity 22.10 poise at 330°F and 28 sec⁻¹.

Table 3

Effects of Additives on Viscosity and Softening Point of H-Coal^a

<u>Additive</u>	<u>Wt. %</u>	<u>Softening Point OF</u>	<u>Brookfield Viscosity^c</u>			<u>% Reduction Viscosity at 330°F</u>
			<u>2789F</u>	<u>3050F</u>	<u>3300F</u>	
None	-	275	-	-	22.10	5.0
Dimethyl Acetamide	5	204	29.33	10.00	5.23	-
Tetramethyl Urea	5	200	7.50	2.77	1.03	-
N-methyl-2- pyrrolidone	5	207	5.05	1.90	1.00	-
Hexamethyl phosphoramide	5	194	13.41	4.92	2.25	-
Methylheptyl Ketone	5	258	b	b	5.30	-

^a Batch 2

^b Two phases

^c At shear rate of 28 sec⁻¹

Table 4

Effect of Concentration of Additive on Viscosity of H-Coal

<u>Additive</u>	<u>Wt. %</u>	<u>H-Coal Batch No.</u>	<u>Brookfield Viscosity</u>		<u>% Reduction</u>
			<u>Poise^a</u>		
			<u>330°F</u>	<u>355°F</u>	
Acetic Anhydride	0	5	-	24.13	-
	1	"	-	14.35	40.5
	2	"	-	11.46	52.5
	4	"	-	9.00	62.7
Propylene Oxide	0	6	-	16.08	-
	2	"	-	6.97	56.7
	4	"	-	4.53	71.8
N-Methyl-2- Pyrrolidone	0	4	37.50	-	-
	1	"	8.10 ^b	-	78.4
	2	"	5.58	-	85.1
	4	"	3.17	-	91.5

^a At shear rate of 28 sec⁻¹

^b Extrapolated from Vis. at 340 and 355°F

Table 5

Effect of Additives on Viscosity of Solvent Refined Coal

<u>Additive</u>	<u>Wt. %</u>	<u>Brookfield Viscosity</u>	<u>% Reduction Viscosity at 440°F</u>
		<u>440°F, 28 sec⁻¹ Poise</u>	
None	-	10.00	-
Propylene Oxide	1.0	8.50	15.00
Acetic Acid	2.0	7.00	30.00
Acetic Anhydride	1.0	6.00	40.00
Aromatic Oils			
2095 Extract	10.0	5.60	44.0
1095 Extract	10.0	2.75	72.5
Light Cycle Oil	10.0	2.20	78.0
Hydrotreated Light Cycle Oil	10.0	1.65	83.5

Table 6

Supplier and Nature of Additives

<u>Additive</u>	<u>Supplier</u>	<u>Chemical Nature or Structure</u>
Naphthenic Acid (200 A.N.)	Atlantic Richfield	A mixture of carboxylic acids containing a cycloparaffinic ring and isolated from naphthenic crude oil. Avg. Mol. Wt. 260.
Acetic Anhydride	Eastman Organic Chemicals	$(\text{CH}_3\text{CO})_2\text{O}$
Dodecetyl Succinic Anhydride	Humphrey Chem. Co.	$\text{C}_{12}\text{H}_{23}-\text{CH}-\text{CO} \begin{array}{l} \\ \text{CH}_2-\text{CO} \end{array} \text{O}$
Propylene Oxide	Union Carbide	$\text{CH}_3-\text{CH}-\text{CH}_2$ \diagdown O
Epoxide No. 7	Procter & Gamble	$\text{ROCH}_2-\text{CH}-\text{CH}_2$ \diagdown O R = n-C ₈ H ₁₇ & n-C ₁₀ H ₂₁
Cocoamine	Armak	Primary amine produced from coconut fatty acids.
Duomeen C	Armak	N-Coco-1,3-propanediamine
Dimethylacetamide	Aldrich	$\text{CH}_3\text{CONMe}_2$
Tetramethylurea	Aldrich	$\text{Me}_2\text{N}-\text{CO}-\text{NMe}_2$
Hexamethyl- phosphoramide	Aldrich	$\text{P}(\text{O})(\text{NMe}_2)_3$
N-methyl- 2-pyrrolidone	GAF	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{CH}_2-\text{C} = \text{O} \\ \diagdown \\ \text{N} \\ \\ \text{Me} \end{array}$
Methylheptyl ketone	Armaour	$n-\text{C}_7\text{H}_{15} \begin{array}{l} \text{C}-\text{Me} \\ \\ \text{O} \end{array}$

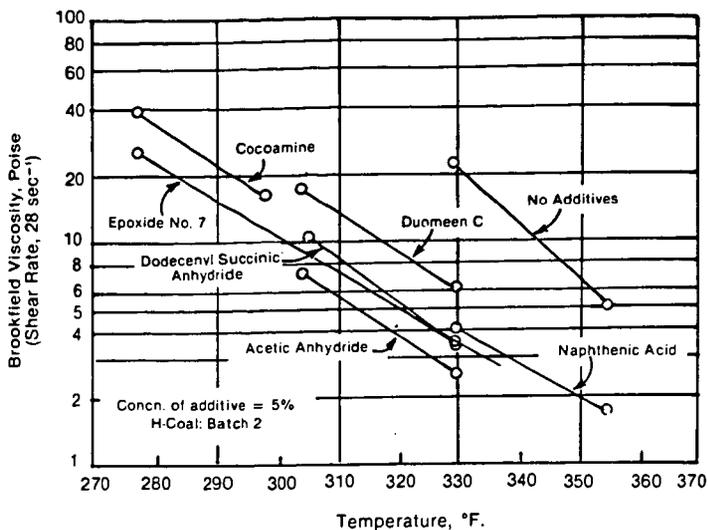


Figure 1. Effect of Additives on Viscosity of H-Coal

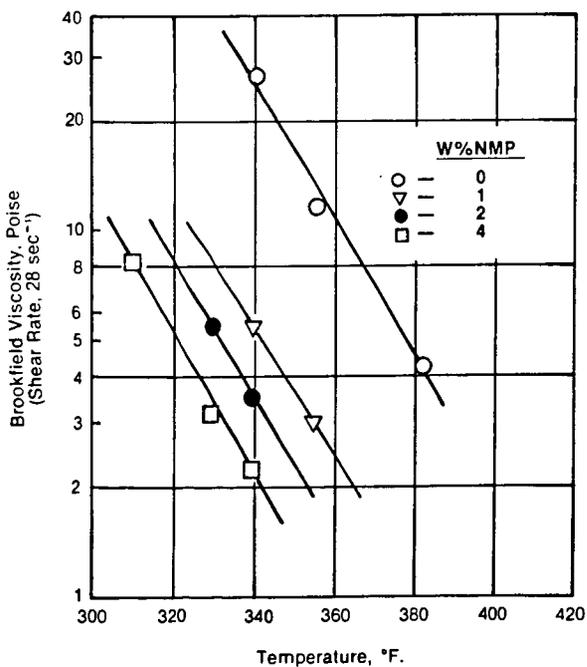


Figure 2. Effect of N-Methyl-2-Pyrrolidone (NMP) on Viscosity of H-Coal (Batch 4)