THE CHEMISTRY OF SHALE OIL AND ITS REFINING

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Contents

Summary

The composition of shale oil depends on the shale from which it was obtained as well as on the retorting method by which it was produced. As compared with petroleum crude, shale oil is heavy, viscous, and is high in nitrogen and oxygen compounds. The oxygen content of shale oils is much higher than in natural petroleum. Low molecular oxygen compounds are mainly phenolics. Carboxylic acids and non-acidic oxygen compounds such as ketones are also present.

The basic nitrogen compounds in shale oils are pyridine, quinoline, acridine, amine and their alkyl substituted derivatives, the weakly basic ones are pyrrole, indole, carbazole and their derivatives, and the nitrile and amide homologues are the non-basic constituents. Sulfur compounds in the shale oils include thiols, sulfides, thiophenes and other miscellaneous sulfur compounds. Elemental sulfur is found in some crude shale oil but is absent in others.

In general, shale oil has a particular and offensive odor derived from the high levels of nitrogen compounds. They are the most deleterious components in shale oil, since they

are well-known catalytic poisons in various refining processes. They cause stability problems in gasoline, jet and diesel fuels, and produce NOx emissions in burners.

Because of these characteristics, further processes are needed to improve the properties of shale oil products. The basic unit operations in the oil refining are distillation, coking, hydrotreating, hydrocracking, catalytic cracking, and reforming. The process selected will largely depend on the availability of equipment and the individual economics of the particular refinery.

Shale oil produced in China was used for producing gasoline, diesel fuel, and wax in the past, but now it is only used directly as fuel. In the US, many commercial tests have been made, using hydrotreating and catalytic cracking processes to obtain light liquid fuels. In Brazil, shale oil is produced on a small scale and liquefied petroleum gas and sulfur are also obtained as by-product.

1. Introduction

Shale oil is a synthetic crude oil produced by retorting oil shale. Compared with petroleum crude, shale oil is heavy, viscous, and is high in nitrogen and oxygen compounds. Shale oil has a rather high specific gravity, approximately 0.9–1.0, owing to the presence of heavy nitrogen-, sulfur-, and oxygen-containing compounds. High pour points are observed and small quantities of arsenic and iron are present. In general, shale oil has a particular and offensive odor, which is derived from the presence of nitrogen compounds, up to an order of magnitude higher than that found in petroleum. They are the most deleterious components of shale oil, since they are well-known catalytic poisons in various refining processes, such as fluid catalytic cracking, catalytic reforming, and catalytic hydrotreating. They cause stability problems in gasoline, jet and diesel fuels, and produce NOx emissions in burners. Finally, their removal is difficult, increasing refining costs significantly.

Other characteristic properties of shale oils are: (1) high levels of olefins and diolefins—which are not present in petroleum crudes—requiring special care during processing due to their tendency to polymerize and form gums; (2) high levels of aromatic compounds, deleterious to kerosene and diesel cuts; (3) high carbon/hydrogen ratio; (4) low sulfur levels, compared with most crudes available in the world (though for some shale oils from the retorting of marine oil shale, high sulfur compounds are present); (5) suspended solids (finely divided rock) which cause process problems chiefly if a first step of processing is hydrotreating; (6) moderate levels of metals.

Because of these particular characteristics, further processes, such as upgrading and refining, are needed to improve the properties of shale oil products.

2. Composition and Properties of Shale Oil

The composition of shale oil depends on the shale from which it was obtained as well as on the retorting method by which it was produced. Of all the possible variables that can affect the quality of shale oil the retorting method is by far the most significant. For example, the specific gravity of shale oil decreases with a rise in cracking temperature.

The major difference in shale oils that are produced by different processing methods is in boiling-point distribution. Rate of heating as well as temperature level and duration of product exposure to high temperature affect product type and yield. Properties of shale oils from various locations are given in Table 1.

The hydrocarbons making up shale oil could be classified as being about 20% alkanes, 20% aromatics, 25% aromatic resins, and 35% olefins and naphthenes. By contrast, a typical crude would contain about 15% alkanes, 50% aromatics, and 35% naphthenes with hardly any olefins or resins.

Location	**Sp gr (API)**	**Elemental analysis (wt %)**					**Analysis of distillate (<350),wt % of <350 ^{0}C cut**		
		C	**H**	**O**	**N**	**S**	**Saturates**	**Olefins**	**Aromatics**
Colorado, US	0.943 (18.6)	84.90	11.50	0.80	2.19	0.61	27	44	29
Kukersite, Estonia	1.010	82.85	9.20	6.79	0.30	0.86	22	25	53
Stuart, Australia		82.70	12.40	3.34	0.91	0.65			
Rundle, Australia	0.636 (0.91)	79.50	11.50	7.60	0.99	0.41	48	2	50
Irati, Brazil	0.919 (22.5)	84.30	12.00	1.96	1.06	0.68	23	41	36
Maoming, China	0.903	84.82	11.40	2.20	1.10	0.48	55	20	25
Fushun, China	0.912	85.39	12.09	0.71	1.27	0.54	38	37	25

Table 1. Properties of shale oils from various locations.

A typical Green River shale oil contains 40 wt % hydrocarbons and 60 wt % organic compounds, which contain nitrogen, sulfur, and oxygen. The nitrogen occurs in ring compounds with nitrogen in the ring, e.g., pyridines, pyridines, pyrroles as well as in nitriles, and it comprises 60 wt % of the non-hydrocarbons' organic components. Another 10 wt % of these components is sulfur compounds, which exist as thiophenes and some sulfides and disulfides. The remaining 30 wt % is oxygen compounds, which occur as phenols and carboxylic acids.

Although the content of asphaltene or resin in shale oil may be low, it is responsible for the dark color as well as the viscosity. Asphaltene in shale oil may be unique since it is high in nitrogen content and, consequently, high in ash content as well. The polarity of the nitrogen polycyclics may also explain the specific properties of emulsification of water and metal complexes.

2.1 Hydrocarbons

The fundamental structure of the organic matter in shale gives rise to significant quantities of waxes consisting of long normal alkanes and the alkanes are distributed throughout the raw shale oil. Retorting processes, which use flash pyrolysis, produce more fragments containing the high-molecular weight, miltiring aromatic structures. Processes that use slower heating conditions, with greater reaction times at low temperature 300–400 °C (570–750 °F), tend to produce higher concentrations of *n*-alkanes. Naphthene-aromatic molecules of intermediate boiling range 200–400 °C (400–750 °F) also tend to be formed with the slower heating processes.

The distributions of saturate hydrocarbons, alkenes, and aromatics in different boiling ranges are also different. Saturated hydrocarbons in the shale oil increase and the aromatics increase slightly with a rise in boiling range, while alkenes decrease with a rise in boiling point. For example, in the light fraction of Fushun shale oil below 350 °C, saturated hydrocarbons account for 38% of total hydrocarbons, while in the heavy fraction of 350–450 °C, they account for 50% with more than two-thirds being normal alkanes. Alkenes in the light and heavy fractions of Fushun shale oil vary from 37% to 22%, and aromatics increase from 25% to 32%.

Saturate hydrocarbons in the shale oil include *n*-alkanes, iso-alkanes, and cycloalkanes, and the alkenes consist of *n*-alkenes, iso-alkenes, and cycloalkenes, while the main components of aromatics are monocyclic, bicyclic, and tricyclic aromatics and their alkyl substituted homologues.

The preferred structures for petroleum refining will necessarily contain higher concentrations of intermediate boiling range waxes of $C_{15–25}$ weight range.

2.2 Oxygen-containing Compounds

The oxygen contents in natural petroleum crudes are generally between 0.1% and 1.0% (wt), whereas the oxygen contents in shale oils are much higher and vary with different shale oils. For example, in the Maoming shale oil, the oxygen content is about 2.2% (wt), while the oxygen content of the Kukersite shale oil is more than 6% (wt), and oxygen-containing compounds account for about 50% (wt) of the whole crude shale oil. The oxygen content varies in different boiling point fractions of the shale oil. In general, it increases as the boiling point increases, and most of the oxygen atoms are concentrated in the high boiling point fraction.

Low molecular phenolic compounds are the main acidic oxygen-containing compounds in the light fraction of the shale oil; for example, 85% (wt) of the phenols in Fushun shale oil concentrated in the <225 °C fraction. Such phenolic compounds are phenol, cresol, dimethyl-phenols, ethyl-phenols, trimethyl-phenols, tetramethyl-phenols. Substituted phenols account for most of the volatile components of the acid fraction. Small amounts of carboxylic acids may also be present in the shale oil. Non-acidic oxygen-containing compounds with a carbonyl functional group such as ketones, indenones, aldehydes, esters, and amides are also present in the <350 °C fraction of the shale oil. Ketones in the shale oil mainly exist as 2- and 3-alkanones. Other oxygen-containing compounds in the <350 °C fraction include alcohols, indenol, naphthol, and ether.

2.3 Nitrogen-containing Compounds

The nitrogen content in the shale oil is relatively higher than in natural crude oil. The nitrogen-containing compounds identified in shale oils can be classified as basic, weakly basic, and non-basic. The basic nitrogen-containing compounds are pyridine, quinoline, acridine, amine and their alkyl substituted derivatives, the weakly basic ones are pyrrole, indole, carbazole and their derivatives, and the nitrile and amide homologues are the non-basic constituents. Most of these compounds are useful chemicals, although some of them are believed to affect the stability of shale oil. Generally, basic nitrogen accounts for about one-half of the total nitrogen, and is evenly distributed in the different boiling point fractions. Nitrogen compounds occur throughout the boiling ranges of the shale oil, but have a decided tendency to exist in high boiling point fractions. Pyrrole-type nitrogen increases with a rise in the boiling point of the shale oil fractions. Porphyrin may occur in the high boiling point fraction of the shale oil.

Of the nitrogen-containing compounds in the <350 °C light shale oil fraction, the majority contain one nitrogen atom. Pyridine and quinoline homologues comprise the majority of the basic nitrogen compounds in Maoming and Fushun light shale oil. Benzoquinolines, principally acridine and alkyl-substituted homologues, could not present significantly in the light shale oil, because the boiling point of benzoquinoline and its alkyl-substituted homologues is higher than 350 °C.

Organic nitrogen-containing compounds in the shale oil poison the catalysts in different catalytic processes. They also contribute to stability problems during storage of shale oil products since they induce polymerization processes, which cause an increase in the viscosity and give rise to the odor and color of the shale oil product.

The high nitrogen content of shale oil asphaltene could affect the mineral or ash content in asphaltenes. This property will also contribute to the surface and colloidal nature of shale oil, which forms emulsions with water.

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Biographical Sketch

Guo Shaohui was born in September 1958. He earned his Master Degree in 1990 and Ph.D. Degree in 1998 at the University of Petroleum, Beijing, China, where he is now a professor and a vice dean of the Faculty of Chemical Engineering. From 1985 to 1995 he studied the oil shale and shale oil chemistry. His MS Thesis was on "Nitro-containing compounds in Chinese light shale oil" and his Ph.D. Dissertation on "Physical and chemical structure of organic matter in immature source rocks and the mechanism of immature petroleum formation." His research activities are now focused on analytical chemistry, petroleum chemistry, and organic geochemistry.