Desulfurization, denitrogenation and deoxygenation of shale oil

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Abstract. *Producing valuable transportation fuels from shale oil has long been a goal among the industries concerned, but to meet modern environmental regulations a significant upgrading is required involving removing heteroatoms from it. The quantity of sulfur, nitrogen and oxygen in shale oil is one of the major obstacles to its wider use. Unlike petroleum whose upgrading consists mainly in desulfurization, for shale oils denitrification and deoxygenation are also important. This review compiles and summarizes the extensive research that has been performed on removing sulfur, nitrogen and oxygen from shale oil. By far the most widely investigated method has been hydrotreatment, but the results of work done with other methods are also presented.*

Keywords: *shale oil, desulfurization, denitrification, deoxygenation, refining, fuel.*

1. Introduction

Shale oil has long been touted as a substitute for conventional petroleum [1]. It is a liquid fuel produced from solid oil shale via a process called pyrolysis [2, 3], and it has been estimated that at least 4.7 trillion barrels of oil could be produced from known deposits [4]. However, technical and environmental challenges have largely kept shale oil production from being economically feasible [5]. Nevertheless, shale oil is currently produced industrially in Brazil, China and Estonia [4], and due to the sheer size of the resources, shale oil continually attracts attention, especially in times when oil prices are high.

Transportation fuels have been produced commercially from shale oil in the past, but not in recent history. During the 1920s, 1930s and 1940s motor fuels were commercially produced in Estonia from oil shale [6, 7]. Likewise,

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motor fuels were produced in China in the 1940s and 1950s [8]. In Australia during World War II transportation fuels were also produced from shale oil to meet wartime demand [9]. Transportation fuels have been commercially produced in South Africa as well [10, 11]. However, these fuels would not meet modern environmental regulations because desulfurization, denitrogenation and deoxygenation were only performed to a minor extent, if at all. For this reason, in more recent history shale oil has mostly been used as a lower value product, e.g. fuel oil or boiler fuel [8, 12].

To produce transportation fuels from shale oil that meet current environmental standards a significant upgrading is needed to remove the large quantities of sulfur, nitrogen and oxygen usually present in oil [13]. Given the importance of removing these heteroatoms, a lot of research has been done on different methods for doing so, with some early studies dating back as far as 1930 [14–16]. Processes for desulfurization, denitrogenation and deoxygenation of shale oil have also been of interest to shale oil companies as a way to add higher value products to their portfolios. For example, Eesti Energia, a shale oil company, recently carried out extensive analysis and pilot plant testing with the goal of producing Euro V diesel from shale oil [17]. Due to the continual interest in shale oil upgrading, we found it important to compile and summarize the existing research on the subject to aid researchers who will work on this problem in the future. Earlier reviews can be found about the removal of heteroatoms from petroleum and biofuels (see, for example, [18, 19]), but shale oil has a different composition and will likely require upgrading pathways that are different from those currently used in refineries [20, 21]. Therefore, here we present what is, to our knowledge, the first thorough review of research on desulfurization, denitrogenation and deoxygenation of shale oil.

2. Composition of shale oil

Kerogen, the main organic structure in oil shale [2, 22–24], is usually described as a three-dimensional macromolecular substance [25]. Oil shale is a broad term, and the structure and composition of its kerogen can vary widely between deposits [26, 27]. The differences between different oil shales, along with differences in the retorting methods used, lead to dissimilarities in the composition and properties between the shale oils produced [28, 29].

Some representative structures have been presented for the kerogens in Kukersite [30], Green River [25, 31, 32] and Rundle [31] oil shales and Guttenberg Member kerogen [30]. Generally, kerogen can be described as consisting of ring structures connected by long straight hydrocarbon chains. Heteroatoms are also distributed throughout the structure. These structural features can often be found in the resulting oil. For example, in Kukersite shale oil a main class of compounds is phenols with straight alkyl side chains [33, 34],

and these structural features can be seen in the representative model of Kukersite kerogen [30]. Due to the structure of kerogen, aromatic compounds are common in many shale oils. Aromatic compounds can also arise due to secondary reactions that occur during pyrolysis [35].

As with other unconventional fuels such as biofuels and coal liquids, shale oil usually contains higher amounts of heteroatoms than conventional petroleum. For conventional petroleum crude the elemental composition generally is the following: 82–88 wt% C, 10–16 wt% H, 0–1 wt% N and 0–6 wt% S, with very little oxygen, if any [36]. Based on literature data we collected on more than 200 crude shale oil samples, the composition of shale oil is mainly the following: 78–86 wt% C, 7–13 wt% H, 0.1–3 wt% N, 0.3–9 wt% S and 0.4–7 wt% O. Figure 1, Figure 2 and Figure 3 depict histograms showing the distribution of petroleum and crude shale oil samples based on the amount of heteroatoms they contain. From this information it can be seen that shale oil generally contains significantly more heteroatoms than crude oil. Also, note that in petroleum the majority of heteroatomic compounds are sulfur compounds, but in shale oil nitrogen and oxygen are also often present in large quantities. Given the large number of heteroatoms, a significant portion of the compounds in shale oil contain heteroatoms. In Green River shale oil, for instance, 61% of the compounds contained a heteroatom [37].

The sulfur compounds often found in shale oil include thiophenes, benzothiophenes, dibenzothiophenes, thioesters and thiols [34, 38–42]. Some disulfides may also be present [40]. The main classes of nitrogen compounds are pyridines, pyrroles, quinolones, carbazoles, indoles, acridines and some nitriles [41, 43–45]. Oxygen compounds include phenols, resorcinols, ketones,
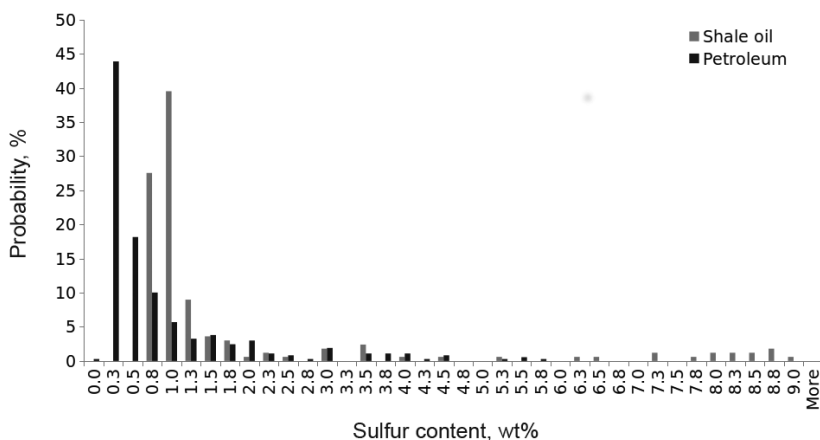

Fig. 1. Distribution of crude shale oil and crude petroleum samples based on sulfur content. Data on crude petroleum are taken from [36].
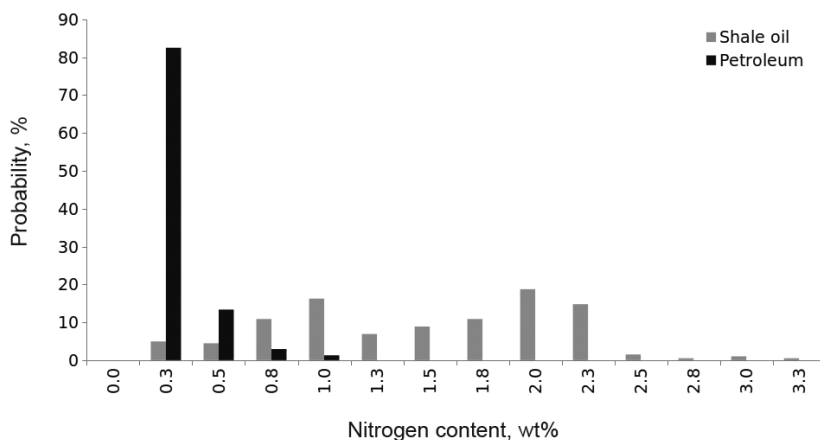
Fig. 2. Distribution of crude shale oil and crude petroleum samples according to nitrogen content. Data on crude petroleum are taken from [36].
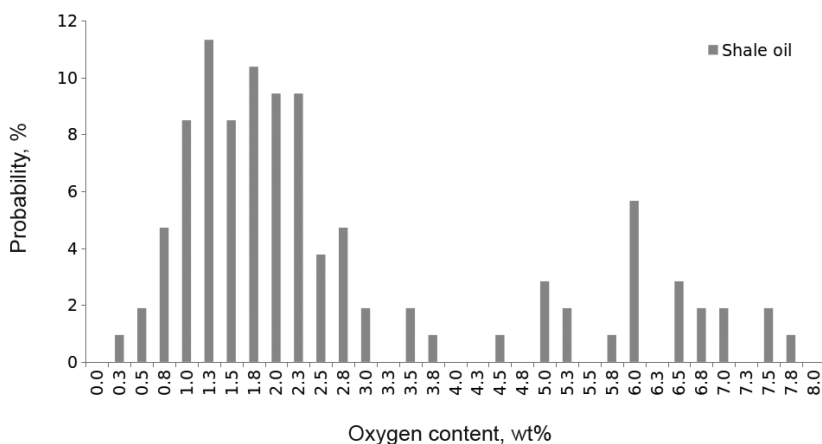

Fig. 3. Distribution of crude shale oil samples based on oxygen content.

organic acids and benzofurans [34, 41, 44]. Hydroxypyridines can also be present [45], and shale oil often contains olefins [34, 37, 41]. As mentioned, the exact composition of a shale oil depends on the composition of the raw oil shale and the retorting/processing methods used, and large differences in composition can be seen between different shale oils.

Another difference between shale oils and conventional petroleum is in the distribution of heteroatoms among different fuel fractions. In conventional

petroleum there is more sulfur and nitrogen in the higher boiling portions of the crude [36]. Although this trend also generally holds for the nitrogen in shale oils, sulfur and oxygen compounds are often most concentrated in lower boiling fractions [33, 37, 46–55]. Thus, separating out lighter portions of shale oil via distillation may actually increase the concentration of heteroatoms in the distillate.

Because the composition of shale oil is different from that of conventional petroleum, the former generally requires refining pathways that are different from those currently used in petroleum refineries [13, 21].

3. Technologies used for removing heteroatoms from shale oil

3.1. Hydrotreatment

By far the most commonly used technology for removing heteroatoms from shale has been hydrotreatment [1, 14–16, 20, 39, 43, 44, 56–102]. In hydrotreating reactions occur between hydrogen and oil in the presence of a catalyst. Hydrogen reacts with unsaturated carbon bonds and heteroatoms, and the latter can then be removed in the form of a gas (H_2S, NH_3 or H_2O). Generally, the reactions are carried out at high temperatures and pressures, often about 300 to 400 °C and 10 to 20 MPa.

Hydrotreatment generally gives a good quality oil and a high yield. The concentrations of heteroatoms in oil can be reduced to quite low levels, but reaching these low concentrations requires severe hydrotreating conditions that may be quite costly. To make the upgrading process more economical, it has often been suggested that hydrotreatment be combined with other methods (such as coking or extraction) or only be used to the point at which oil can be used as a feedstock for a conventional refinery [69, 83, 84].

Most studies have been performed using autoclaves or fixed bed reactors. Some processes have employed an ebullated bed reactor, which represents a three-phase fluidized bed reactor [72–74, 79, 91]. A trickle bed reactor has also been used by some researchers [88, 103, 104]. This type of reactor similarly involves three phases, but the solid phase is stationary. A few processes have employed multistage reactors as well [20, 56–58, 86, 92].

A variety of different catalysts, often commercial ones, have been used. On many occasions, the exact composition and properties of the catalyst have not been given. Some common metals used in the catalysts include Co, Ni, W and Mo along with silica and alumina. Early studies also investigated using reduced iron ore [14, 15], and Shamsi [105] studied the catalytic properties of the mineral portion of oil shale.

Several studies have combined coking with hydrotreatment in an attempt to increase process efficiency. In the coking process a fuel is heated until thermal decomposition occurs, which leads to the production of smaller molecules that are recovered as a liquid or gas and a solid carbon residue called coke [106].

Note that these studies have used coking as a treatment step, so the coking began with shale oil, not raw oil shale. One advantage of using coking with shale oil is that any solids or metals remain in the residue from the coking process, making it easier to further refine the remaining liquid fuel [84]. In the late 1940s the United States Bureau of Mines constructed a small refinery that used coking (thermal cracking) as the first step [21]. For delayed coking with recycle they reported yields of 40.6 vol% gasoline and 39.1 vol% light gas oil. Distillates from the coking unit were further treated by extraction with basic and acidic solutions to remove some of the sulfur and nitrogen compounds. Similar coking experiments were also performed at about the same time by Egloff et al. [10, 107].

Sullivan and Stangeland [82] also investigated using coking as the first step in upgrading shale oil. They reported a 77.9% yield of C_5 + liquid and a coke yield of 18.3%. They then further processed the liquid fuel in a hydrotreating pilot plant. The researchers noted that the coking-hydrotreating process was less costly than other refining processes investigated by them. However, the process was claimed to be "the least energy efficient in the production of transportation fuels".

Shale oil has generally not been upgraded at an industrial scale. Two known exceptions are hydrocracking and hydrogenation performed at the Fushun oil shale plants in China in the 1950s [8] and a commercial scale test performed by the Standard Oil of Ohio in conjunction with the United States Navy in the late 1970s [90, 94]. Although both were reported to be successful, the upgrading activities were not sustained long term. In China the refinery built for shale oil was instead used for refining petroleum [8]. In the test for the U.S. Navy some problems occurred because FeS_x deposited in the guard bed used before the hydrotreating unit, which led to the shutting down of the process due to a high pressure drop across the bed. Despite the complications, 73,100 barrels of shale oil was hydrotreated.

3.2. Catalytic cracking

Unlike hydrotreating, which largely just saturates carbon bonds and removes heteroatoms, catalytic cracking processes are designed to break carbon bonds in the fuel to form smaller molecules. A few processes used fluid catalytic cracking or hydrocracking as one of the upgrading steps [8, 44, 82–85, 95, 107]. Many studies reviewed for this article seemed to only have the goal of upgrading shale oil enough that it could be used as a feedstock for a conventional refinery. This may explain why catalytic cracking has generally not been used because any need to crack the fuel would be handled in a conventional refinery.

3.3. Extraction and adsorption

One way to remove undesired compounds is via extraction or adsorption. Several of the patents on oil shale upgrading processes involve extraction

steps [70, 71, 80, 81, 108]. After first coking shale oil, Qian and Tian [8] used extraction steps to remove oxygen- and nitrogen-containing compounds from it. Lankford and Morris [21] used a similar process, and Han et al. [109] also removed nitrogen compounds using acidic reagents. Luik et al. [59–65] removed phenolic compounds from shale oil before hydrotreating it. Often a liquid solvent serves as an extracting agent, but some studies have used solid agents, for instance, $CuCl_2 \cdot xH_2O$ or hydrated iron (III) chloride to remove nitrogen compounds [110–112].

Bunger [47] has suggested that extracting some compounds from oil can be economically beneficial if these can be sold as higher value products. At the same time, both Qian and Tian [8] and Lankford and Morris [21] gave this as a reason for extracting heteroatomic compounds. Indeed, in Estonia Viru Keemia Grupp and their predecessors have long recovered water soluble phenols from shale oil to sell or convert to more valuable products [113], and during the Soviet period research was performed to find different ways of using these phenols [114]. However, extraction or adsorption is usually combined with other upgrading methods because on its own it does not reduce the sulfur and nitrogen content to a low enough level, as can be seen from the work by Chi et al. [108].

In addition to the work done on removing sulfur, nitrogen and oxygen, Curtin et al. [69] developed a method to remove arsenic from shale oil. Arsenic can poison catalysts used in hydrotreatment, and it is often desirable to remove it as well. The researchers then used a guard bed filled with the adsorbent to protect the catalyst in the hydrotreater. In the commercial scale test performed at the Standard Oil of Ohio, a guard bed was also used to protect the hydrotreatment unit [90].

3.4. Hydroretorting

Shale oil is produced from solid oil shale via pyrolysis in a process called retorting. Some studies and patents have proposed upgrading during the retorting process itself by adding a hydrogen source [16, 115–124]. An advantage of using this method is that almost all of the organic matter in oil shale can be recovered. This is significant because usually in retorting some portion of organic matter forms a solid residue called semi-coke, which remains in oil shale. For some types of oil shale only a relatively low proportion of organic matter can be recovered using traditional retorting methods. However, hydroretorting can afford oil yields similar to those of high yield oil shales [117]. Krichko [118] cited a 96–98% conversion of the shale organic matter to liquid or gaseous products.

Hydroretorting can result in a shale oil with a lower content of heteroatoms. Though, Krichko [118] showed that a significant amount of heteroatoms can still remain in oil. He stated the sulfur content in the gasoline fraction was 0.6–0.7%. This suggests that hydroretorting may not be as effective as

hydrotreatment in removing heteroatoms. Changing process conditions, however, may allow better removal of heteroatomic atoms. Abbasian et al. [119], for instance, demonstrated it is possible to capture the H_2S formed during hydroretorting directly in the reactor by adding a solid sorbent (limestone or siderite).

It is possible to separate the organic matter in oil shale, called kerogen [2, 22], from the mineral material by using a process named floatation [115, 117, 125]. Some of the hydroretorting studies have employed this concentrated kerogen (organic content 80–90%). Tippin and Rex [117] proposed using this floatation technique in commercial hydroretorting operations.

The majority of hydroretorting studies have used hydrogen gas, but the patents by McCollum and Quick [120, 121] describe employing a water-containing fluid at supercritical conditions. It appears that the fluid acts as a source of hydrogen for the reactions, and a catalyst is also added to the fluid to promote the conversion process. The patent reveals that the fluid also included organic solvents that could dissolve the shale oil compounds produced during pyrolysis. In addition, the authors stated that their retorting process could remove sulfur compounds and metals from the oil.

Oil shale can be mined and retorted above ground, or it can be retorted within the oil shale formation itself using in situ retorting. Therefore, in situ upgrading techniques have also been proposed in some patents [120–123]. Sometimes the upgrading was performed by pumping hydrogen into the formation during in situ retorting. McCollum and Quick [120, 121] also stated that their method could be used in situ by pumping the fluid directly into the oil shale formation.

It is worth mentioning that changing the retorting conditions, even without adding hydrogen, can also affect the amount of heteroatoms in the resulting shale oil. Elenurm et al. [54] showed this in a pilot-scale solid heat carrier retort, and Oja et al. [55] investigated this in a Fischer assay retort. Although the concentration of heteroatoms generally cannot be reduced to low levels without adding hydrogen, choosing appropriate retorting conditions may make desulfurization, denitrogenation and deoxygenation more efficient.

4. Hydrotreatment chemistry

4.1. Changes in shale oil composition

A common theme throughout the studies reviewed was that nitrogen compounds are more difficult to remove than sulfur compounds when hydrotreating shale oil. Studies which used milder hydrotreating conditions showed relatively low removal rates, although even at mild conditions most of the sulfur was removed. Landau [13] summarized this by saying that when

comparing the difficulty of removing different heteroatoms from shale oil S < O << N, and tentatively stated that the concentrations of S, O and N in the hydrotreated products could be reduced to < 0.05/< 0.1/< 0.5 wt% at "normal" hydrotreating conditions.

One possible reason for an easier removal of sulfur is that shale oil generally does not contain significant quantities of dibenzothiophenes, which are present in larger quantities in crude oil and are more difficult to remove [13, 34, 44, 126]. In addition, Rollmann [126] indicated that when hydrotreating heterocyclic sulfur compounds sulfur will be eliminated in the form of hydrogen sulfide without hydrogenation of the aromatic ring. However, for heterocyclic nitrogen and oxygen compounds hydrogenation seems to be required prior to C-N or C-O bond scission [126, 127]. Oxygen compounds have proved to be more easily removed via hydrotreating than nitrogen, with the oxygen content being reduced significantly at even mild processing conditions [13, 43, 44].

Among nitrogen compounds those contained in ring structures, such as pyrrole, carbazole and pyridine derivatives, are generally the most difficult to remove [13, 128]. Holmes and Thompson [45] indicated that the most difficult compounds to remove are hindered pyrroles and alkylpyridines. Souza et al. [44] also showed that pyridines, quinolines, indoles and carbazoles still remained in large quantities in the hydrotreated oil. Experiments by Chen et al. [77] demonstrated that most compounds after hydrotreatment contained one nitrogen atom and double bond equivalents of 4 to 10. The basic compounds identified were pyridine derivatives. Harvey et al. [43] also stated that pyrroles were less reactive, at the same time, they reported that pyridines were removed to a significant extent. For further information about the removal of heteroatoms from fuels the reader is referred to excellent reviews by Girgis and Gates [129] and Landau [13].

Hydrogenation of double bonds and aromatic rings is another set of chemical reactions that occur when hydrotreating shale oil. The H/C ratio of the fuel increases. Double bonds are saturated fairly rapidly [44]. With aromatic compounds, Afonso et al. [91] determined that the major reactions are partial hydrogenation of aromatic rings and cracking of alkyl side chains. Some studies have also shown that the concentrations of some aromatic compounds can actually increase during hydrotreating [43, 44, 89]. Harvey et al. [43] performed hydrotreatment in different reactors and with different catalysts, and their results indicate that the reactions occurring with aromatic compounds during hydrotreatment can vary significantly depending on the catalyst and processing conditions.

For hydroretorting processes the findings of Burnham and Happe [35] are significant. During pyrolysis/retorting a secondary process that occurs is the conversion of aliphatic hydrocarbons to aromatic hydrocarbons. The researchers found hydrogen to inhibit this process. Therefore, hydroretorting has the potential to produce a shale oil with lower aromaticity.

4.2. Notes about catalysts

Although we do not attempt to thoroughly analyze and compare the different catalysts used (which could be the subject of a separate review), a few findings about these substances are worth mentioning.

The high concentrations of nitrogen in many shale oils can deactivate some catalysts, such as those in fluid catalytic cracking units, and so it may be important to select a catalyst that is not deactivated by nitrogen and sulfur. The H-Oil process carried out in an ebullated bed reactor used such a catalyst [74]. Arsenic, which is present in higher concentrations in many shale oils, can also deactivate catalysts, and its removal may be necessary [69].

Shamsi [105] investigated the catalytic activity of oil shale minerals in hydrodesulfurization reactions by introducing thiophene into a reactor containing the minerals. He showed that almost all the oil shale minerals were catalytically active to some extent, and for some of the minerals more than 50% of the thiophene was converted at higher temperatures. Therefore, the oil shale minerals present during the retorting process likely have an effect on the composition of the shale oil produced, and this was also shown by Elenurm et al. [54] and Oja et al. [55].

The effectiveness of different catalysts was compared by Benson [130], and of the 12 catalysts studied, the HF-activated Co molybdate gave the best results. Other studies have also shown that increasing the acidity of the catalyst by adding halogens improves their ability to remove nitrogen [13]. For a more detailed discussion of the catalysts used in hydrotreating shale oil the reader is referred to the review by Landau [13].

5. Conclusions

It seems likely that hydrotreatment is necessary to reduce the concentrations of heteroatoms in shale oil to acceptable levels. However, using other upgrading methods in addition to hydrotreating may help to improve a refinery's economic performance, for instance, by reducing the cost of the hydrotreatment step. It has been stated that it is economically more beneficial to upgrade fuel only to the point that it could be used as a conventional refinery feed stock.

The review also reveals that nitrogen, especially those contained in ring structures, is the most difficult heteroatom to remove from the fuel during hydrotreatment.

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