Oil Shale, Vol. 12, No. 1
pp. 39-45

ISSN 0208-198X

https://doi.org/10.3176/oil.1995.1.04

ICHTHYOL PRODUCTION FROM ISRAELI SHALE OIL

V. FAINBERG
G. HETSRONI
S. LEICHTER

Centre for Research in Energy Engineering
and Environmental Conservation,
Faculty of Mechanical Engineering,
Technion - Israel Institute of Technology,
Haifa, Israel

PAMA (Energy Resources Development) Ltd.,
Mishor Rotem, Israel

Methods of ichthyol production from the Israeli shale oil are investigated. Ichthyol (ichthammol) is an anti-inflammation and analgesic remedy, used for curing skin diseases. The scheme developed includes the following steps: purification of the oil fraction; sulfonation of the fraction; neutralization of the sulfonic acids by ammonium hydroxide; purification of the crude ichthyol. The ichthyol yield is 170--250 % of the initial fraction (75-120 % of the total oil). The ichthyol obtained meets requirements of the British Pharmacopoeia. Simplicity of the synthesis, high yield, and high price for ichthyol make its production economically favourable.

Ichthyol (it is also called ichthammol, etc.) is an anti-inflammation and analgesic remedy, obtained from shale oils. It is applied for curing skin diseases such as eczema, ulcers, furuncles, etc. It is used in creams, ointments, bandages, and lotions, often with zinc oxide. Different remedies of ichthyol type are used now in Germany, Spain, Britain, Austria, Switzerland, Australia, etc. [1]. Some modifications of ichthyol are also employed as veterinary remedies.

Ichthyol looks like a dark viscous liquid, soluble in water and glycerin. From the point of view of a chemist ichthyol is an aqueous solution of ammonia salts of sulfonic acids, in which thiophene compounds are dissolved. Healing properties of ichthyol are explained by the presence of sulfur compounds. The sulfonic acids, which are the basic components of ichthyol, have an emulsifying effect and communicate to the product a capacity to soak into the skin.

Ichthyol is produced for more than 100 years in Austria and also in Russia. Ichthyol of a high quality can be obtained only from high-sulfur oil shales. That is the reason why it is produced only in these two countries which have deposits of suitable shales. The Austrian oil shale (so-called "red stone") contains 11.5-54.5 % of organic matter and 17-18 % of sulfur. Shale is retorted at a temperature of 500 °C and at a pressure of 0.5-2.5 kg/m^2 in small transportable ovens with a capacity of 120-

-140 kg. The oil yield is 10-20 %. The oil contains about 13 % of sulfur [2]. In the 1970s, intensive investigations were carried out in Austria aimed to study the prime matter for ichthyol (shale oil) and to raise the quality of this product [3, 4]. Various modifications of ichthyol have been obtained, for instance ichthoform - a combination of ichthyol with formaldehyde. An attempt was made to produce an ichthyol-like product ("Tumenol") from the oil of the Messel oil shale deposit, Germany; this oil contains only 0.52 % of sulfur. In 1987 the oil shale obtained from France was processed in Austria in order to investigate a possibility of producing ichthammol from it [5]. The ichthyol price at the world market is about 25,000 USD per ton (1994).

The specific feature of the Israeli shale oil is a high content of hetero-atoms - more than 10 %, mainly of sulfur [6]. The determining role of sulfur in the shale oil composition is confirmed by Aizenshtat [7]. Using mass spectrometry he identified 135 compounds in the shale oil, most of them sulfur compounds of alkyl-thiophene type. Alkyl-thiophenes are present within a broad boiling range from C_1 up to C_{20} and constitute a dominating part of the shale oil sulfur compounds.

A high content of thiophene compounds and relatively low cost of production make the Israeli shale oil a good resource for ichthyol production.

Experimental

The 200-300 °C shale oil fraction was chosen as a prime matter for a preliminary investigation of the methods of ichthyol production. The choice of the upper limit of the boiling point was based on the following considerations:

1. The prime matter must contain as much organic sulfur as possible. Dependence of sulfur content on the boiling point of the shale oil fraction is shown in Fig. 1. One can see that sulfur content decreases with increasing the boiling point. That is why the use of an oil residue with a boiling point above 300 °C is not desirable.

2. Specifications for the medical ichthyol require a complete absence of phenols in the product. This condition cannot be fulfilled when too heavy prime matter is used, because the completeness of the phenol extraction drops sharply with increase in the fraction boiling point.

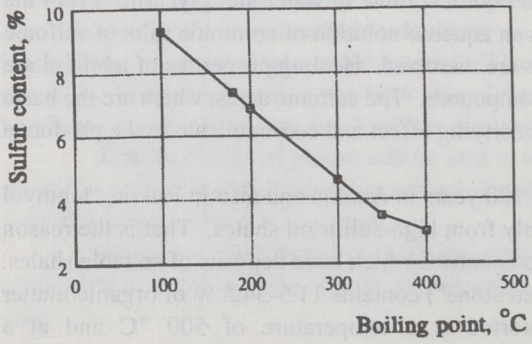

Fig. 1. Relation between the fraction boiling point and sulfur content

3. Heavy oil fractions contain aromatic structures with condensed rings, which may have carcinogenic nature. As it has been known, the concentration of the condensed-ring compounds rises sharply when the boiling point exceeds 300 °C.

4. The most important stage of the ichthyol production is the sulfonation of the oil fraction. The heavy products are sulfonated under harder conditions than the light ones. When a fraction with a too broad boiling range is treated it is difficult to get a completely sulfonated product.

These four reasons dictate the use of a fraction which boils up to temperatures not exceeding 300 °C. As to the lower limit of the fraction boiling point, there are no principal obstacles for using low-boiling fraction for ichthyol synthesis. However, from the chemical point of view a fraction with a narrower boiling range might be more favourable for the ichthyol production. Therefore the 200-300 °C oil fraction was chosen as a prime matter for obtaining ichthyol.

Characteristics of the initial oil and the 200-300 °C fraction used for the ichthyol production are shown in Table 1.

After preliminary investigations the following scheme of ichthyol production was chosen:

- purification of the fraction;
- sulfonation of the fraction;
- neutralization of the sulfonic acids obtained by ammonium hydroxide;
- separation of the ammonium salts of the sulfonic acids (crude ichthyol) from aqueous phase;
- purification of the crude ichthyol.

Purification of the fraction. The first stage in obtaining ichthyol is purification of the fraction aimed to remove undesirable components from it, mainly phenols and pyridine bases. It is to note that the odour of the purified fraction is weaker and less unpleasant than that of the initial product.

Table 1. **Characteristics of Shale Oil for Ichthyol Production**

Characteristics	Total oil	200-300 °C fraction
Fraction yield, wt. %	100	40.3
Density at 15 °C	0.9827	0.956
Viscosity at 50 °C, cSt	11.57	2.35
Bromine value	76	87.6
Elemental analysis, %:		
C	79.53	79.79
H	9.74	10.64
O	2.20	0.48
N	1.52	1.58
S	6.81	7.61
Molecular mass	213	185
Insoluble, % wt.:		
in heptane	1.78	0.5
in toluene	0.04	0
Moisture, %	1.0	0

Ichthyol synthesis. The chemical process of ichthyol synthesis may be presented by the following main reactions:

$$\underset{\text{fraction}}{RH} + H_2SO_4 = \underset{\text{sulfonic acids}}{RSO_3OH} + H_2O \text{ (sulfonation)}$$

$$RSO_3OH + NH_4OH = \underset{\text{ichthyol}}{RSO_3ONH_4} + H_2O \text{ (neutralization)}$$

Since an excess of the acid is always used for sulfonation, the aqueous phase contains besides water significant amounts of ammonium sulfate.

In reality, the process of sulfonation is much more complicated. Different groups and compounds of shale oil fraction react with sulfuric acid in a different way. Generally, sulfuric compounds, such as thiophenes, react with sulfuric acid in the first turn. After that unsaturated hydrocarbons participate in the reaction of sulfonation, then aromatics follow. Naphthenes and paraffins are sulfonated in the last turn or are not sulfonated at all.

The most important parameters of the sulfonation process are concentration and quantity of sulfuric acid, temperature, and duration of the synthesis. The higher the acid concentration, the higher the degree of the sulfonation (Fig. 2). However, the acid of a high concentration may cause oxidation of the oil compounds with formation of SO_2, polymerization of thiophenes, etc. [8]. When reacting with unsaturated hydrocarbons, sulfuric acid may produce alcohols. It is known that thiophenes and mercaptans are apt to polymerize in the presence of sulfuric acid and form resin-like substances, which deteriorate the quality of the end products.

Washing sulfonic acids with water. Sulfonic acids are practically insoluble in water, whereas the excess of sulfuric acid is washed out of the sulfonation products. Due to this operation, consumption of ammoniac for neutralization (see below) decreases, and the content of ammonium sulfate in ichthyol also decreases. Since sulfuric acid is removed from the mixture, neutralization (it is an exothermic

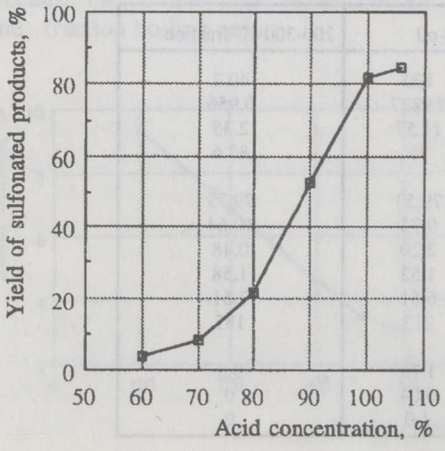

Fig. 2. Yield of sulfonation products vs. acid concentration

reaction) may take place at a lower temperature. Some quantity of unsulfonated components in ichthyol, determined by means of extraction, was 25-35 %. It was already mentioned that the presence of some quantity of unsulfonated compounds is desirable in ichthyol.

Preparing Ichthyol from Sulfonic Acids. Sulfonic acids were neutralized by NH_4OH solution. The upper layer was the crude ichthyol - a dark, very viscous, almost hard mass, and the lower one - the aqueous solution of ammonium sulfate and ammonium hydroxide. Ichthyol solubility in water is limited, and it decreases if the aqueous phase contains inorganic ions, such as salts, etc. Therefore, ichthyol can be easily separated from the aqueous phase. Unsulfonated components are also partly separated at this stage.

Water and traces of ammonia were evaporated from the product up to the dry mass content of 50-55 %. The resulting product was ichthyol.

Ichthyol Yield. The ichthyol yield was as it is shown in Table 2.

Table 2. **Ichthyol Yield, %**

Yield	On the purified fraction	On the initial fraction	On the total oil
Yield of dry ichthyol	84	71	36
Yield of commmercial ichthyol (water content 50 %)	168	142	71

Table 3. **Results of Sulfur Determination in Ichthyol (% on dry matter)**

Type of sulfur	Requirements of the Pharmacopoeia	Content in the obtained ichthyol
Total	–	15.8
Organic	Not less than 10.5 %	14.1
Sulfates	No more than 25 % of the total S	1.7 (10.7 % of the total S)

Ichthyol Quality. Ichthyol, obtained from the Israel shale oil, in every respect meets the requirements of the British Pharmacopoeia [9]. The most important characteristics is its sulfur content (Table 3).

The pure, concentrated ichthyol *per se* is not applied as a remedy. It is used in ointments and lotions in concentrations of 5-10 %. In order to evaluate the behaviour of the Israeli ichthyol in medical preparations and compare it with the product sold on the world market, ointments, containing the German ichthyol (production of the Deutsche Ichthyol Gesellshaft, Hamburg) and the ichthyol obtained in our laboratory, were prepared according to the requirements of the British Pharmacopoeia. Both the ointments had similar properties. The odour of the ichthyol ointment is characteristic, but not strong and not disagreeable. When a small amount of a deodorant additive is introduced into the ointment, it acquires a light agreeable odour.

Conclusion

Methods of ichthyol production from the Israeli shale oil were developed. The scheme developed includes the following steps: purification of the oil fraction; sulfonation of the fraction; neutralization of the sulfonic acids by ammonium hydroxide; purification of the crude ichthyol. The ichthyol yield is 170-250 % based on the initial fraction (75-120 % on the total oil). The ichthyol obtained meets the requirements of the British Pharmacopoeia. Simplicity of the synthesis, high yield and high price for ichthyol make its production economically favourable.

Acknowledgements

This research was supported by PAMA (Energy Resources Development) Ltd. It was also supported by the Center for Absorption in Science, Ministry of Immigrants Absorption, State of Israel, and by the Wolfson Family Charitable Trust Program for the Absorption of Immigrant Scientists. Support was also received from the Technion Vice-President for Research and the Mexico Foundation.

ПОЛУЧЕНИЕ ИХТИОЛА ИЗ ИЗРАИЛЬСКОЙ СЛАНЦЕВОЙ СМОЛЫ

В. ФАЙНБЕРГ, Г. ХЕЦРОНИ, С. ЛАЙХТЕР

Резюме

Исследованы методы получения ихтиола из израильской сланцевой смолы.

Разработанная схема включает следующие операции: выбор и получение оптимальной фракции; очистка фракции от фенолов и азотистых оснований; сульфирование фракции; нейтрализация; очистка сырого ихтиола.

Выход ихтиола 170—250 % на фракцию (75—120 % на суммарную смолу).

REFERENCES

1. *Martindale W.* The Extra Pharmacopoeia. 1988.
2. Ullmann's Encyclopedie der technischen Chemie. B. 13. 1962. S. 35-42.
3. *Pailer M et al.* Untersuchung stark schwefelhaltiger Schieferöle // Monatshefte für Chemie. B. 104. S. 297; 313; 339.
4. *Pailer M et al.* Untersuchung stark schwefelhaltiger Schieferöle // Monatshefte für Chemie. 1965. B. 96. H. 4. S. 1377-1406.
5. *Knutson C. F. et al.* Developments in the oil shale in 1987 // The AAPG Bull. V. 72. No 10B, October 1988. P. 378-390.

6. *Fainberg V., Podorozhansky M., Laichter S., Hetsroni G.* Oxygen and nitrogen compounds of Israeli shale oil // Fuel Science & Technology International. 1994. Vol. 12, No 4. P. 581-592.
7. *Aizenshtat Z.* Thermal behaviour and products of various rocks deposits as a tool of better optimization of its future utilization // The Hebrew University report. 1992.
8. *Stadnikov G. L.* Investigation of the Kashpir shale oil in connection with ichthyol production // Proceedings of Karpov Inst. 1930. P. 175-190 (in Russian).
9. British Pharmacopoeia. 1988. P. 308.

Presented by V. Yefimov
Received November 04, 1994