Impact Factor:					
	ISRA (India) = 6.317	SIS (USA) = 0.912	ICV (Poland) = 6.630
	ISI (Dubai, UAE) = 1.582	РИНЦ (Russia) = 3.939	PIF (India) = 1.940
	GIF (Australia) = 0.564	ESJI (KZ) = 9.035	IBI (India) = 4.260
	JIF = 1.500	SJIF (Morocco) = 7.184	OAJI (USA) = 0.350

SOI: 1.1/TAS DOI: 10.15863/TAS

International Scientific Journal

Theoretical & Applied Science

p-ISSN: 2308-4944 (print) **e-ISSN:** 2409-0085 (online)

Year: 2021 **Issue:** 11 **Volume:** 103

Published: 10.11.2021 **http://T-Science.org**

QR – Issue QR – Article

David V. Roytman
unemployed
researcher

A.A. Yusif-zadeh
unemployed
researcher

F.M. Farzalizadeh
unemployed
researcher
kerem_shixaliyev@mail.ru

PRODUCTION OF THIOPHENE FROM THE PYROLYSIS GAS OF THE JANGICHAY SHALE

Abstract: *In this work, preparation of thiophene and its homologues from the products obtained during the pyrolysis of the Jangichay oil shale of Azerbaijan is considered. As is known, thiophene is used to obtain physiologically active compounds, drugs, herbicides and other substances. Recently, the main source of production of thiophene and its homologues is the coke industry, but this source does not meet the demand for thiophene.*

Key words: *thiophene, oil shale, pyrolysis, gas, tar, organic carbon, extract, thermogravimetric analysis.*

Language: *English*

Citation: Roytman, D. V., Yusif-zadeh, A. A., & Farzalizadeh, F. M. (2021). Production of thiophene from the pyrolysis gas of the Jangichay shale. *ISJ Theoretical & Applied Science, 11 (103)*, 389-392.

Soi: http://s-o-i.org/1.1/TAS-11-103-34 ***Doi***: https://dx.doi.org/10.15863/TAS.2021.11.103.34

Scopus ASCC: *1600.*

Introduction

UDC 662.67.66.092.174:3:543:1

Research on possible substitutes for oil has increased recently. Countries such as Australia and Scotland use oil shales to obtain products similar to those from oil.[1] About 60 shale deposits have been discovered in Azerbaijan, but the possibility of using them as energy fuel remains unexplored due to the presence of significant oil and gas reserves. [2].

Thermal processing of oil shale produces significant quantities of thiophene and its derivatives. Thiophene is used to obtain photochromic materials, physiologically active compounds, drugs, optical elements for solar cells, herbicides, etc.

If we take into consideration that 1 kilogram of thiophene and its compounds cost about 1000 US dollars, the production of thiophene from oil shale is an environmentally friendly process. [3-5]

For the research, Jangichay shale was taken. Fischer analysis, elemental and technical analysis were carried out for this shale. The type of kerogen and its chemical composition were determined.

Fischer analysis showed that the composition of shale includes: tar – 14.75%, solid residue – 71.54%, decomposition water – 2.62%, gas – 11.09% of the mass.

According to the elemental analysis, the amount of total carbon is 21.93%, of which 1.23% is of carbonates and, probably, comprises the mineral part of the shale. Organic carbon is 20.7% and together with hydrogen, nitrogen and organic sulfur forms the basis of kerogen. [4]

Part of the organic carbon remains in the solid residue due to compaction reactions. We have established that the Jangichay shale belongs to the 2nd (mixed) type. The technical analysis determined the density – 2250 kg/m^3, humidity – 2.84% wt., the

content of volatiles – 22.63% wt., ash – 71.54%, and heat of combustion – 9850 KJ/kg. To determine the chemical composition of kerogen, we used N-methylpyrrolidone extraction. [6-12]

Method

The extract yield for the Jangichay shale was 6.4%. The main part of the extract was made up of oils, which were 75.4%. The rest were of asphaltenes and tars. Studies have shown that in kerogens, there are hydrocarbons that consist of 20 carbon atoms, and there are about 221 aromatic isoprenoids of the alkane series.

Jangichay oil shale was subjected to pyrolysis. The material balance at a temperature of 700°C is given in Table 1.

Table 1. Material balance of Jangichay oil shale pyrolysis.

Taken:	Yield, % mass.
1. Shale Oil	100.0
Total	100.0
Produced:	
1. Gas	0.78
2. Liquid part	91.98
3. Spent shale	6.42
4. Loss	0.82
Total	100.0

Results

Figure 1 shows the thermogravimetric analysis of the pyrolysis of the Jangichay oil shale.

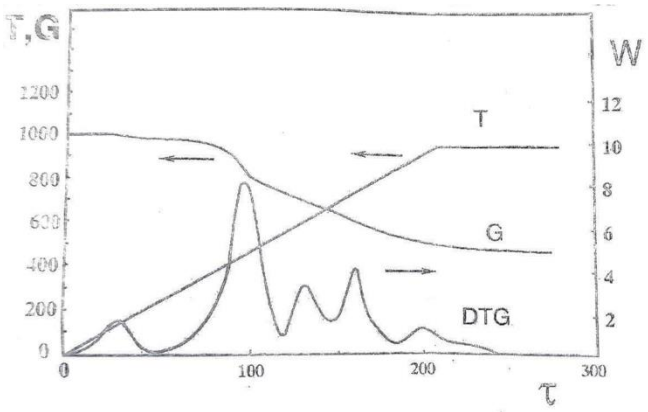

Fig. 1. Thermogravimetric Analysis Data.

As is seen in Figure 1, there are four different regions of sample weight loss.

Loss of mass of the sample due to moisture removal occurred at 120-200°C. Weight loss at 400°C with a maximum at 440°C indicated pyrolytic decomposition of kerogen. The observed weight loss at 520°C was due to the occurrence of secondary decomposition-compaction reactions of the heavy part of the kerogen decomposition products. Weight loss at temperatures above 650°C was due to the mineral matrix, primarily of the decomposition of carbonates.

According to the values of the degrees of conversion calculated by the formula

$$-\ln[-(ln(1-x))'/T^2] \text{ versus } 1/T,$$

a graph of the dependence 2 is built (Fig 2). Two linear sections with different slopes indicate the occurrence of two different reactions in the temperature range of 300-520°C. The primary reactions of decomposition of kerogen proceed at 280-380°C, and secondary processes at 380-520°C, which is consistent with the literature data. [7]

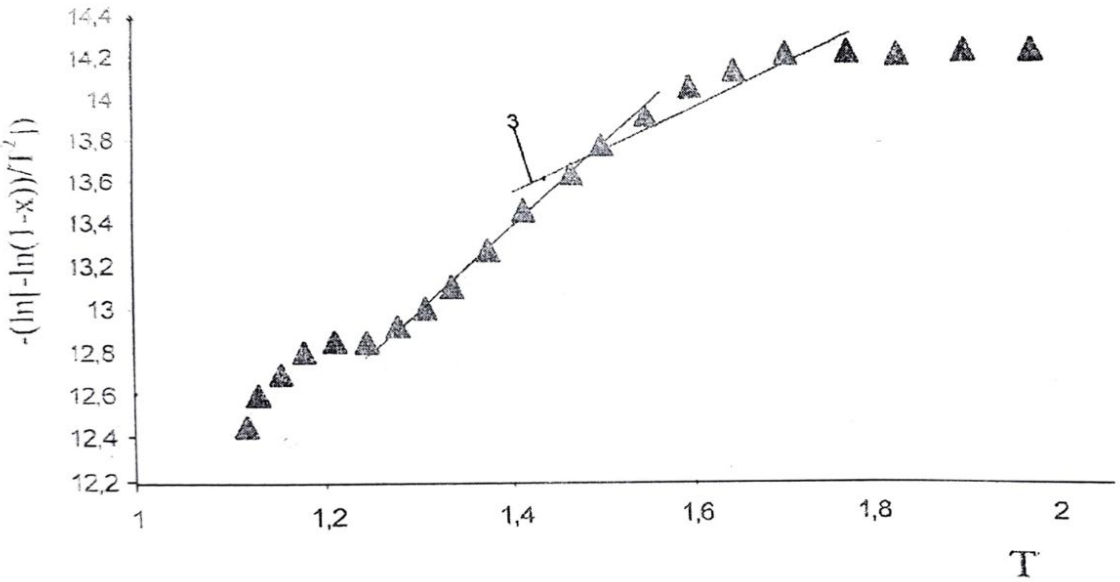

Fig. 2. Graph of the dependence -ln[$-(ln(1-x))'/T^2$] versus 1/T

From this graph, one can determine the activation energy by the slope of the straight line from the reciprocal temperature. The activation energy of primary reactions (E_1) is 13.95 kJ/mol, and the activation of secondary reactions (E_2) is 29.86 kJ/mol.

The decomposition-compaction reactions of primary pyrolysis products with higher activation energies E_2 proceed at temperatures above 380℃ with the formation of final decomposition products. The composition of the Jangichay shale pyrolysis gas is shown in Table 2.

Table 2. Composition of the pyrolysis gas

Components	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	H_2S
Composition % mass	0,5	1,5	14,5	12,5	11,5	8,5	7,0	4,0	11,4	16,6	12,0

We carried out the formation of thiophene by heterocyclization of hydrogen sulphide, which allows us to protect the environment from pollution, and also allows us to improve the main indicators of oil shale processing. To obtain thiophene from gas, a catalyst was prepared, which was first used in Germany. (8.9) The catalyst has the following composition: Al_2O_3 – 10% масс., SiO_2 – 84%, Fe_2O_3 – 5,4%, K_2O – 0,4%, Na_2O – 0,2 % of the mass.

All of these products were ground in a laboratory mill and mixed with 250 ml of distilled water. The resulting mixture was dried at 105 ℃ for 24 hours, after which it was calcined at 500 ℃. The catalyst was loaded into a reactor to which a condenser-cooler was connected. Pyrolysis gases were passed through the reactor at 650 ℃. The resulting catalyst was analyzed on an HP6890 chromatograph. The analysis results are given in Table 3.

Table 3. Catalyst composition

Temperature, ℃	H_2S, %		Composition of the catalyst, % by weight				
	From reactor		Thiophene	2-Methylthiophene	3-Methylthiophene	Benzene	Toluene
	Before	After					
600℃	10,0	2.5	53,4	14,2	6,4	19,4	6,8
650℃	8,0	0,2	75,7	1,2	5,0	12,4	5,7

As can be seen from in Table 3, at 650℃, 75.7% of thiophene and 6.2% of its homologues are obtained. Besides, benzene and toluene are obtained in the composition of the catalyzate. The rest of H_2S makes up 0.2%, that is, the conversion is 98.34%.

Table 4 shows the chemical composition of the pyrolysis tar boiling within the range of the beginning of boiling (b.b.) – 205℃.

Table 4. Fraction composition b.b. – 205℃.

№	Component	% of yield per fraction
1	Benzene	36,5
2	Tiophene	14,1
3	Methyltiophene	24,27
4	Toluene	6,43
5	Ethylbenzene and xylenes	5,4
6	Other components	13,3

Conclusions

As can be seen from the Table 4, the light fractions of the pyrolysis tar contain 38.37% of thiophene compounds, which makes it expedient to use them as raw materials for the extraction of thiophene-aromatic concentrate by the method technologically designed on an industrial scale. (10)

Thus, it was possible to obtain thiophene and its homologues from the pyrolysis gas of Jangichay oil shale of Azerbaijan by heterocyclization of hydrogen sulfide on a catalyst used in Germany.

References:

1. Blokhin, A.I., Nikitin, A.N., & Fraiman, G.B. (2000). Combustible Shale - an alternative fuel and raw material for chemistry. *Fuel and energy complex*, Moscow, № 2, pp.19-25.
2. (1998). *Oil shale of Azerbaijan*. (p.124). Baku: Publishing House of the Institute of Geology of the Academy of Sciences of Azerbaijan.
3. Strizhakova, Yu.A. (2008). *Oil shale. Genesis, compositions, resources*. (p.192). Moscow.
4. Kerimov, Kh.M. (2006). Chromatographic study of oil shale of Azerbaijan deposits. *Journal of chemical problems*, Baku, № 1, pp.46 - 49.
5. Kerimov, Kh.M. (2006). Extraction of oil shale with N-methylpyrrolidone. *Journal of chemical problems*, Baku, № 2, pp.374 - 376.
6. Yusif-zade, A.A., Mamedkhanova, S.A., & Dadayeva, G. Ch. (2020). Investigation of some physicochemical properties of inflannable shale of Azerbaijan. *Theoretical & Applied Science*, Philadelphia USA, issue 02, volume 82, pp. 44 - 47. Soi: http://s-o-i.org/1.1/TAS-02-82-9 Doi: https://dx.doi.org/10.15863/TAS.2020.02.82.9
7. Robinson, W.E., & Cook, G. L. (n.d.). *Compositional Variations of the Organic Material of Green River Oil Chal Colorado.* No. 1 Core - U.S. Bur. Mines. Rep. Invest - 7492 - 1971.
8. Ballice, L., Yuksel, M., & Shulzh, et al. (1995). Application of infrared sprectroscopu to the classification of kerogen types and the Thermogravimetrically Deverol Pyrolysis Kinetic of Oil Shales. *Fuel*, 74, pp.11618 - 1623.
9. Schulzh, H., & Boringev, W. (1984). Kohec. Entwicklung und Anwendung der Kapillar G.G. Gesamtprobenchik fur Gas. *Dampf Vielstoffgemiche, Deutche Forschungbericht*, Hambourg, v. 320, pp. 4 - 20.
10. Prelatov, V.G., & Kashirsky, V.G. (1989). Pyrolysis of high-sulfur shale resin. *Oil shale industry - Inform.* Ser. 1, No. 2, pp. 5 - 6.
11. Shixaliyev, K. (2020). Application of Heavy Metal Ions Separation from Contaminated Water in Industry. *International Journal of Innovative Technology and Exploring Engineering* (IJITEE). Volume-9, Issue-6, April 2020. pp. 132-134. ISSN: 2278-3075, Scopus Link: https://www.scopus.com/sourceid/21100889409 https://www.ijitee.org/download/volume-9-issue-6/ www.ijitee.org
12. Shixaliyev, K. (2020). Retrieval Number: F3070049620 / 2020 © BEIESP DOI: 10.35940/ ijitee. F3070.049620 Propeties of the Composition Based on modified Polyethylenes. ... *International journal of Innovative Technology and Exploring Engineering*, Volume-9, Januaru 2020, pp.2484-2493.