THIOPHENE CATALYTIC SYNTHESIS FROM A BY-PRODUCT OF HYDROCARBON FEED DEMERCAPTANIZATION

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Abstract

Developed is a method of thiophene catalytic synthesis from dialkyl disulfides and C_4-hydrocarbons. This method allows to utilize organic disulfides produced as multi-tonnage wastes during hydrocarbon feed demercaptanization and to produce thiophene - a valuable organic product - from them. At selected optimal conditions the method provides thiophene yield of up to 90 wt %. Developed also is a new composition of polyfunctional magnesia - chromia – alumina catalyst modified with potassium and/or lanthanum oxides for the process of thiophene synthesis from dialkyl disulfides and C_4-hydrocarbons.

Key words: *disulfide oil, catalyst, thiophene*

1. INTRODUCTION

Increasing interest expressed lately to thiophene and its homologues is caused by a possibility of synthesis on its basis of a range of valuable drugs for medicine and veterinary as well as chemicals for agriculture (herbicides and pesticides), conducting and light-emitting polymers, dyes and bleaching agents, additives for lubrication oils, and antiknocks [1-3].

Obvious drawbacks of methods of thiophene synthesis used in modern world practice are the low economic efficiency, which is primarily due to the use of expensive reagent materials, and an insufficient selectivity of the reactions. All of these factors result in a high production cost of the target product-thiophene.

Scientific, experimental and industrial experience of thiophene production shows that selection of feed for thiophene synthesis is of great importance use of available cheap and convenient from the technologic point of view feed simplifies the problem of implementation of a developed process.

Detailed analysis of investigations and industrial developments in this field shows that use of disulfide oil as a feed for thiophene production is grounded both from scientific and technologic points of view. Currently disulfide oil is an unused multitonnage by-product of gas and oil feed demercaptanization which requires to be disposed [4].

2. MATERIALS AND METHODS

Sulfur - containing feed used for study of thiophene synthesis process was: fraction I.B. 167ºC of disulfide oil from gas condensate demercaptanization plant (Orenburg GPZ) containing (wt %): dimethyl disulfide - 3.18, methyl ethyl disulfide - 24.76, diethyl disulfide - 41.60 and ethyl iso-propyl disulfide - 15.16; disulfide oil from propane - butane demercaptanization plant (Orenburg GPZ) containing (wt %) dimethyl disulfide - 69.69, methyl ethyl disulfide - 24.54 and diethyl disulfide - 3.15.

Hydrocarbon feed components used for kinetic studies of thiophene synthesis was n-butane fraction containing 88.0 wt % of *n*-butane

To study and develop processes of catalytic synthesis of thiophene from disulfide oil and n-butane a laboratory and pilot plants were developed and built.

The reaction mixture was analyzed chromatographically in the on-line mode with LKhM-80 gas chromatograph equipped with a thermal conductivity detector, a 3000×3 mm column packed with 10 % 1,2,3-tris-β-cyanoethoxypropane on diatomaceous earth, and ATsP-E24 (L-Card) analog-to-digital converter; the data acquisition and processing program was NetChrom 2.1.

The yield of thiophene was determined according to the following formula in terms of n-butane fed:

$Y = [\ C_{C4H4S} / C_{C4H10}] \cdot 100$, wt %,

where C_{C4H4S} is the mass fraction of thiophene in the products (g/g),

C_{C4H10} – is the mass fraction of *n*-butane in the reagents (g/g).

A special catalytic system containing chromia and magnesia as an active component and potassium and/or lanthanum oxides as a promoter of the general formula: $t Mg_{1-n}Cu_nCr_2O_4$-$xMgO$-yK_2O-zLa_2O_3/Al_2O_3, where *t* lies in the range 5 – 25 wt %, *x*, *y* and *z* are at most 3.2, 2 и 10 wt %, respectively, and the value of *n* ranges within 0 – 1, was designed for the thiophene synthesis.

The catalyst $tMg_{1-n}Cu_nCr_2O_4$-$xMgO$-yK_2O-zLa_2O_3/Al_2O_3 contains X-ray-amorphous phase of magnesium and/or copper chromate, $Mg_{1-n}Cu_nCr_2O_4$, and γ- or (γ+χ)-Al_2O_3 phases promoted by potassium, lanthanum and/or magnesium oxides. Additional introduction of magnesia into chromia – alumina catalyst promoted by potassium oxide and formation of X-ray-amorphous phase of magnesium and /or copper chromate, containing Cr^{3+} cations, provides decrease of cracking capability of the catalyst and coking [5].

In order to increase activity and stability of the catalyst it was subject to preliminary sulfidizing with dimethyl disulfide in hydrogen medium at a temperature of 450 ºC.

3. DISCUSSION OF THE RESULTS

3.1. Thermodynamic calculation of thiophene synthesis process

For determination of an equilibrium composition of a gas mixture at interaction of disulfide oil and *n*-butane and optimal conditions of thiophene synthesis thermodynamic calculation using «IVTANTERMO» program was carried out. Calculation of an equilibrium composition of the gas mixture was performed using the following key components: dimethyl disulfides (DMDS), diethyl disulfide (DEDS), H_2S, S_2, thiophene, CH_4, C_2H_6, C_3H_8, *n*-butane, ethylene, propylene, cyclopropane, cyclobutane, cyclobutene, 1-butylene, iso-butylene, 1,3-butadiene, hydrogen. These basic components were selected on the basis of the assumption about possible composition of products of disulfide oil and n-butane interaction.

The equilibrium composition of the reaction mixture was calculated in the temperature interval from 300 to 1000 K, at a pressure of 0.1 MPa and at reagent composition variation.

It was determined that at DMDS interaction with *n*-butane in equimolar ratio in the temperature interval from 300 to 600 K predominantly methane, hydrogen sulfide and thiophene were observed to be formed in the quantities of 0.56, 0.25 and 0.19 mole fractions respectively (Fig.1). The temperature increase to 1000 K results in hydrogen appearance in the mixture and in decrease of methane and hydrogen sulfide concentrations, while thiophene concentration does not practically depend on temperature.

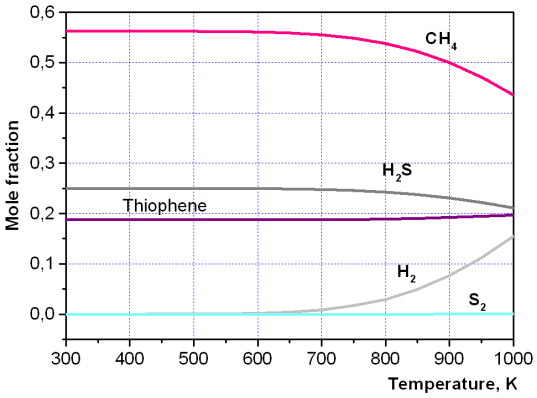

Fig.1. Dependence of the reaction mixture composition on temperature at interaction of 1 mole DMDS and 1 mole of *n*-butane

In case of n-butane interaction with DEDS increase of methane and thiophene concentration and decrease of hydrogen sulfide concentration is observed in the equilibrium mixture as compared to DMDS. This fact allows to assume that use of real disulfide oil, containing high dialkyl disulfides, provides increase of equilibrium yield of thiophene as a reaction product.

It was also found that increase of a molar ratio C_4-hydrocarbon/$C_2H_6S_2$ from 0.5 to 3 results in increase of equilibrium concentrations of CH_4 and thiophene and in sharp decrease of H_2S concentration. Maximal equilibrium thiophene concentration is observed at a ratio of C_4-hydrocarbon/ $C_2H_6S_2$ = 2 and constitutes approximately 0.4 mole fractions of thiophene and does not practically depend on temperature.

Thus scientifically substantiated recommendations were obtained for choosing optimal conditions for thiophene synthesis, i.e. temperature of 600 – 870 K and initial reagents ratio of *n*-butane /DSO in the range of 1-2 (vol.).

3.2. Study of thiophene catalytic synthesis process

As follows from the experimental data (Fig.2) on varying the temperature in the range 300 – 650 ºC, the formation of thiophene from fraction I.B. -167 ºC of DSO and *n*-butane takes place only at temperatures above 450 ºC. In noticeable amounts (more than 50 wt %), thiophene is formed beginning from 550 ºC and reaches its maximum yield of 90 wt % at 580 ºC. The elevation of the temperature above 600 ºC does not produce a favorable effect: on the contrary, the catalyst is quickly deactivated. The rapid deactivation of the catalyst at temperatures above 600 ºC is associated with its coking due to the acceleration of the dehydrogenation reaction.

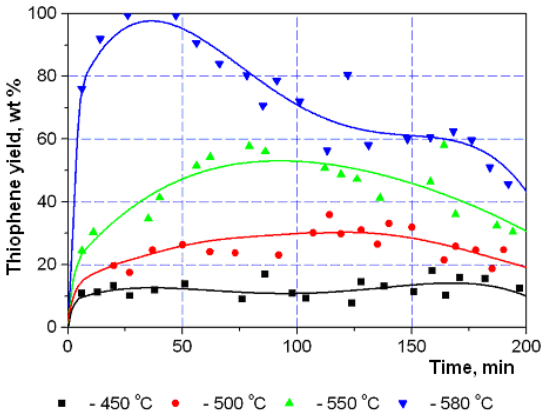

Fig.2. Influence of temperature on the yield of thiophene from *n*-butane and DSO: the DSO : n-butane volume ratio is 1 : 1, the reactant concentration in helium is 10 vol. %

One of the most important stages of the research is study of a volume ratio of *n*-butane : disulfide oil. Data of Fig.3 show that independent of feed components increase of the volume ratio of *n*-butane : DSO from 1 to 2 decreases practically twice the thiophene yield calculated on the fed *n*-butane.

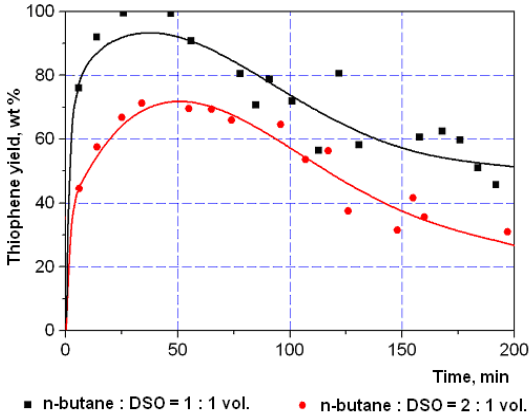

Fig.3. Dependence of the thiophene yield on the ratio of *n*-butane to DSO at 580°C and reactant concentration in helium of 10 vol %.

An increase of initial reactants concentration in gas-carrier (helium) from 10 to 30 % vol. decreases significantly the thiophene yield from 90 to 50 wt % (Fig.3). Taking into account high dehydration ability of the developed polyfunctional catalyst the decrease of the thiophene yield at the reactants concentration increase can be explained by rapid catalyst deactivation due to coking the catalyst surface by condensed dehydrated hydrocarbon fragments, concentration of which increases with the increase of working reactants concentration in the gas - carrier.

On the basis of the results of investigations concerning the influence of the main parameters (temperature, concentration and reactant ratio) on the catalytic activity, we conducted three-cycle experiments on thiophene synthesis from *n*-butane and DSO in the synthesis-regeneration mode.

As follows from the results of the study of thiophene synthesis from disulfide oil the magnesia-chromia-alumina catalyst makes it possible to maintain the thiophene yield at a level of 60-90 wt % during 2 hours; afterwards, the yield of thiophene gradually decreases (to 30-40 wt %).

To recover the catalytic activity, the catalyst was subject to oxidative regeneration with air oxygen at 580 °C.

It follows from the analysis of the results obtained in the second and the third cycle that the catalyst almost completely recovers its catalytic properties after regeneration.

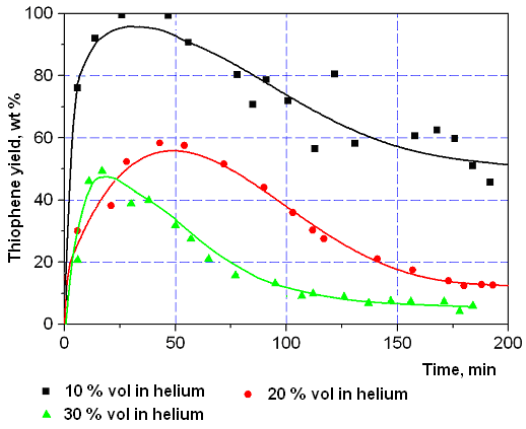

Fig.4. Dependence of the thiophene yield on the concentration of *n*-butane and DSO in helium at 580 °C and a DSO : *n*-butane volume ratio of 1 : 1.

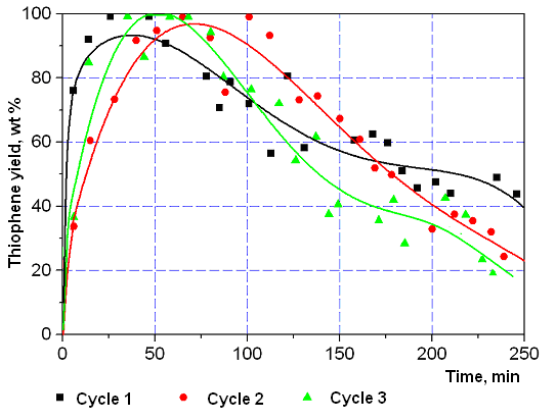

Fig.5. The yield of thiophene during its synthesis from *n*-butane and DSO: reactant concentration of the reactants in helium is 10 vol %, temperature is 580 °C, and DSO : *n*-butane = 1 : 1 (vol)

An analysis of composition and concentration of the equilibrium mixture components showed that in thiophene synthesis from n-butane and disulfide oil predominantly methane, thiophene and hydrogen sulphide are produced. The obtained experimental data agree with the results of calculations performed with the use of «IVTANTERMO» program.

Study of the reaction of thiophene synthesis from *n*-butane and DSO over the developed magnesia-chromia-alumina catalyst showed that the activation energy of the process in the considered temperature interval of 450-580 ºC and in the initial period of the reaction was 2295 J/mole. This value of seeming activation energy shows that the reaction proceeds in an external diffusion region. In this case the reaction velocity is limited by the velocity of the reactants diffusion to the external surface of grains, the reaction velocity being in direct proportionality to the total external surface of the drains in a bed.

The optimal conditions of thiophene synthesis from DSO and *n*-butane determined during laboratory studies are as follows: T=580 ºC, ratio of DSO to *n*-butane = 1 : 1 (vol.), concentration of feed reactants in the gas-carrier - 10% vol. These conditions were used in pilot tests on a unit with a capacity of 500g/hr of DSO.

In order to increase the target product yield and life time of the catalyst a reactor with a fluidized catalyst bed was used in the pilot tests. The advantages of such reactors are high heat transfer coefficient (~1000 W/(m^2·K), high heat conductivity of the bed and lower undesired effect of external diffusion typical for a fixed bed.

The results of the pilot experiments showed that under the conditions of synthesis selected previously, at stable «fluidization» of the catalyst bed, created by gas-carrier (nitrogen), and constant optimal temperature gradient in the reaction zone it is possible to produce a catalyzate containing 34 wt % of thiophene calculated on liquid catalyzate.

To recover the thiophene the catalyzate was subject to laboratory distillation on the basis of a standard method. As a result a thiophene concentrate was obtained with 80 wt % of thiophene. Table 1 shows the component composition of the catalyzate fractions after the distillation.

The data of the table show that contrary to laboratory tests the product of the synthesis is a complex multicomponent mixture containing aromatic hydrocarbons, primary and secondary dialkyl disulfides, methyl and ethyl thiophenes and a significant amount of carbon disulfide (about 35 wt % calculated on catalyzate).

This difference in compositions of thiophene synthesis products in laboratory and pilot tests can probably be explained by the fact that thiophene synthesis in the pilot reactor was accompanied by severe cracking that was proved by high content of carbon disulfide in the catalyzate. Formation of the carbon disulfide can be explained by sulfur interaction with carbon, which was formed during hydrocarbon cracking on the catalyst [7].

A source of the sulfur can be both the sulfidized catalyst surface and cracked dialkyl disulfides under the catalysis conditions.

Prevalence of the process of the reaction mixture components cracking over the processes of heterocyclization and dehydration can be a result of the fact that in the laboratory studies a catalyst with 1.5 mm grains was used, whereas in the pilot tests the size of the catalyst grains was 0.8 mm.

Increase of total external catalyst surface not only increased a velocity of the thiophene synthesis reaction but also resulted in increased reactants cracking to carbon and sulfur due to significant increase of the contact time, their excess on the active surface and, accordingly in their interaction with formation of carbon disulfide.

Table 1 – The component composition of the catalyzate fractions after the distillation

Components	Concentration, wt %				Component yield calculation on catalyzate, wt %
	Fr. 1 40÷70 °C	Fr. 2 70÷90 °C	Fr. 3 90÷100 °C	Fr. 4 > 100 °C	
CS_2	84.19	9.06	2.87	0.01	36.48
CH_3SH	0.09	0.03	0.02	0.04	0.05
C_2H_5SH	0.01	0.16	0.35	0.03	0.12
Mercaptans C_{3+}	0.01	0.05	0.09	2.65	0.56
Dialkyl sulfide C_{2+}	2.18	0.32	0.13	0.24	1.02
DMDS	0.29	4.97	24.97	34.91	11.74
MEDS	-	0.03	0.99	2.93	0.72
Methyl iso-propyl disulfide	-	-	0.34	1.73	0.39
DEDS	-	-	0.01	0.04	0.01
Thiophene	12.61	80.42	43.24	8.84	34.04
Methyl thiophene	0.12	2.02	15.47	28.39	8.31
Ethyl thiophene	-	0.02	1.34	8.08	1.81
Alkanes C_{5+}	0.41	2.36	9.05	10.64	4.12
Aromatic hydrocarbons C_6-C_7	0.09	0.56	1.13	1.47	0.63
∑	100	100	100	100	100
Yield fractions calculated on catalyzate, wt %	40	27	13	20	100

3. CONCLUSION

On the basis of the studies performed it was found that individual dialkyl disulfides and disulfide oil can be used for thiophene catalytic synthesis. The process proceeds over the developed magnesia-chromia-alumina catalyst, modified with potassium and lanthanum oxides, the thiophene yield depending mainly on the reaction conditions and insignificantly on molecular mass of alkyl radicals in the initial dialkyl disulfides. Under the optimal laboratory conditions in a stationary regime: temperature of 580 °C, concentration of feed reactants 10 % vol in gas-carrier, a ratio of DSO : *n*-butane =1:1 (vol) and the contact time of 2 sec the developed method provides up to 90 wt % thiophene yield calculated on the fed *n*-butane.

The pilot experiments is a fluidized bed of small-spheric catalyst of similar chemical composition showed that it is possible at the same time to produce and separate two valuable organic sulfur products (carbon disulfide and thiophene) in the form of a 80 wt % concentrate.

REFERENCES

1. L. Belenkiy, E. Zakharov, M. Kalik. New Trends in Thiophene Chemistry. Moscow 1976; 424.
2. I. Nasyrov, I. Numanov. Syntheses on the Basis of Benzothiophenes. Proceedings of the III Republic Scientific and Technical Conference on Petrochemistry. Guriev 1977; 9: 2152-54.
3. I. Foigt. Stabilization of Synthetic Polymers Against Light and Heat Effect. Leningrad 1972; 544.
4. S. Yashnik, Z. Ismagilov, S. Khairulin, A. Mazgarov, A. Kopylov, A. Vildanov, R. Sadykov. The Catalyst and Process of Thiophene Production. 2008. Russian patent RU 2 325 228 C1.
5. S. Borisenkova, A.Vildanov, A. Mazgarov. Contemporary Problems of Oil and Petroleum Products Desulfurization. Russian Chemical Journal 1995; 39; 5: 87-101.
6. M. Ryashentseva, A. Pogorelov, E. Belanova, R. Merzhanova. Thiophene Synthesis from Butane and Hydrogen Sulfide over Rhenium Catalysts. Neftekhimia 1973; 13: 6: 840-44.