

Steam cracking of hydrocarbons

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Steam Cracking of Hydrocarbons. 5. Effect of Thiophene on Reaction Kinetics and Coking

Martin Bajus, Václav Veselý, and Jozef Baxa

Department of Chemistry and Technology of Petroleum, Slovak Technical University, Jánska Ul. 1, 880 37 Bratislava, Czechoslovakia

Piet A. Leclercq* and Jacques A. Rijks

Laboratory of Instrumental Analysis, Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

The effect of thiophene on the kinetics and selectivity of the conversion of hydrocarbons by steam cracking was studied in a stainless steel tubular reactor with relatively large inner surface. Heptane was selected as a model and decomposed at 700 °C and 100 kPa with a mass ratio of steam to feed of 3:1. The rate of decomposition increased about 14% if 0.1 and 0.5% mass of thiophene was added, but was unchanged if 1% was present. The influence of thiophene on the selectivity of the conversion of heptane to ethene appeared to depend on the residence time. The effect of thiophene on the formation of coke was investigated in the pyrolysis of a reformer raffinate in a stainless steel flow reactor at 820 °C, without steam. Coking is lessened with increasing amounts of thiophene in the feed (0.05–0.5% mass). Reaction mechanisms are suggested.

Introduction

Sulfur compounds can influence the course of radical reactions in the thermal decomposition of hydrocarbons to olefins. They can be introduced into the reaction system either independently, that is before the pyrolysis of the hydrocarbon, or together with the feed. In the first case gaseous sulfur compounds are often used. These compounds react with the inner surface of metal reactors to give metal sulfides. The passivation of a stainless steel reactor surface by the action of hydrogen sulfide, for instance, inhibits the course of secondary reactions which are leading to the formation of coke in the pyrolysis of propane (Crynes and Albright, 1969), ethane (Dunkleman and Albright, 1976), and propene (Ghaly and Crynes, 1976). Pyrolysis after sulfiding the surface produces more ethene, less hydrogen and carbon monoxide from ethane, and less hydrogen and methane from propene.

Furthermore, sulfur compounds also influence the reactions in the gaseous phase, as illustrated with hydrogen sulfide in the pyrolysis of 2-methyl-2-pentene (Frech et al., 1976) and piperlylenes (Hutchings et al., 1976). While the mechanism of isoprene formation from 2-methyl-2-pentene does not change, a change of mechanism does occur in the formation of byproducts, such as 2-methyl-1-pentene, methylpentadiene, and 4-methyl-2-pentene. With piperlylenes the dominant reaction is cyclization to cyclopentadiene and decomposition to butadiene. In the thermal decomposition of 3-methyl-*cis*-2-pentene an increase in the initial rate of decomposition and a decrease of isomerization to 2,3-dimethyl-1-butene were observed (Gousty and Martin, 1974).

Dehydrogenation properties of both sulfur and sulfur dioxide were used during heating of propane (Lang, 1967) to propene. Elemental sulfur causes not only marked inhibition of coking, but also an acceleration of the conversion of hydrocarbons (Bajus and Veselý, 1980).

The purpose of this work is to gain information on the influence of thiophene on the kinetics of conversion of hydrocarbons and on yields of products. Thiophene was chosen rather than elemental sulfur, hydrogen sulfide, and

other substances which were investigated before and which by decomposition give radicals of the type $\cdot\text{SH}$. Thiophene is a sterically nonhindered, nonsubstituted heteroarene able either to inhibit pyrolysis as an aromate, e.g. benzene, or support it as some sulfur substances investigated before.

Materials and Methods

The thermal decomposition of heptane and reformer raffinate were investigated in the presence and absence of thiophene. Stainless steel tubular reactors of the flow type with enlarged inner surface were used.

The experimental equipment, in which the kinetics of the conversion was studied, was described previously (Bajus et al., 1979). The reactor is of the "tube-in-tube" type with a surface-to-volume (S/V) ratio of 6.65 cm^{-1} . The stainless steel reactor was of the following composition (% mass): Cr, 16.8; Ni, 10.7; Mn, 1.1; C, 0.08. The starting hydrocarbon, heptane (Loba-Chemie Wien, 99.7%), was introduced at 0.15–0.35 mol h^{-1} . The work was carried out at 700 °C in the presence of steam. Under the effective contribution of the inner surface, steam reacts with some reaction components, especially with high molecular weight compounds which are the potential precursors of coke, to carbon monoxide and hydrogen. Steam also ensured the reproducibility of the measurements and enabled the equipment to be used continuously without the necessity of burning carbonaceous deposits. The mass ratio of water to heptane was in all experiments 3:1. The amount of water varied between 2.57 and 5.85 mol h^{-1} .

The formation of coke was studied in the flow equipment described previously (Bajus and Veselý, 1980). The tubular reactor is of the U type, with $S/V = 6.66 \text{ cm}^{-1}$. The construction material is stainless steel (% mass): Cr, 12.5; Ni, 9.4; Mn, 0.7; C, 0.18. The influence of thiophene on the formation of coke was studied in the pyrolysis of a reformate raffinate, obtained from the catalytic reforming of naphtha after extraction of aromatics. This raffinate had the following composition (% mass): unbranched alkanes, 18.8; branched alkanes, 60.4; cycloalkanes, 10.3; aromatics, 6.0; remaining products, 4.5. Its flow was 0.30 mol h^{-1} in all experiments. The pyrolysis was carried out

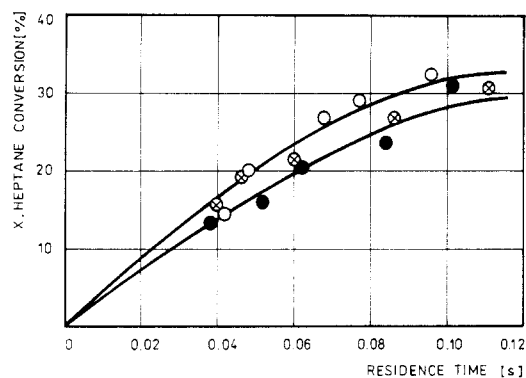


Figure 1. Conversion of heptane as a function of residence time at different thiophene contents (% mass): ○, 0.5; ⊗, 0.1; ●, 1.0.

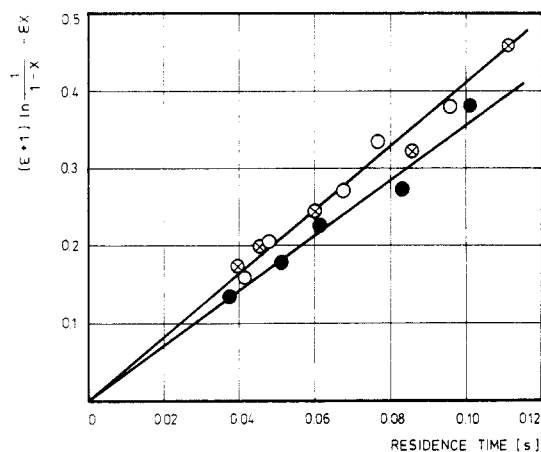


Figure 2. Graphic representation of the first order rate equation at different thiophene contents (% mass): ⊗, 0.1; ○, 0.5; ●, 1.0.

without steam at 820 °C and 100 kPa. The amount of coke formed was determined by weighing the reactor before and after the experiment. In order to achieve reproducible results, the preparation of the reactor before each experiment is of prime importance. Burning out the coke from the preceding experiment with air and decomposition of metal oxides by the action of a solution of acids (3% HCl + 3% H₂SO₄) preceded each run.

The equivalent volume V_R of the reactors was determined from the thermal profile of the nonisothermic reactors according to Hougen and Watson (1947). The residence times were determined as described previously (Bajus et al., 1979).

The composition of the gaseous and liquid product mixtures was determined by gas chromatography by methods reported previously (Bajus et al., 1979; Bajus and Veselý, 1980).

Results

Kinetics of Thermal Decomposition. Heptane, admixed with 0.1, 0.5, and 1% mass of thiophene, was decomposed at 700 °C at residence times of 0.02–0.12 s. Rate constants were determined with the assumption that decomposition is an irreversible reaction of the first order occurring in a stationary reactor with plug flow (Bajus et al., 1979).

The dependence of the conversion of heptane on the residence time for different concentrations of thiophene is illustrated in Figure 1. The right-hand term of the rate equation ($k\tau$) as a function of residence time for the corresponding amounts of thiophene is plotted in Figure 2. The values of the rate constants determined graphically and calculated numerically are given in Table I. This table also contains the rate constant of the conversion of heptane without thiophene, determined at 700 °C under the same

Table I. Rate Constants of the Heptane Conversion at 700 °C

thiophene content, % mass	$k_{anal.}$, s ⁻¹	$k_{graph.}$, s ⁻¹
0	3.68 ^a	3.6 ^a
0.1	4.08	4.1
0.5	4.05	4.1
1.0	3.58	3.6

^a From Bajus et al. (1979).

Table II. Gas Production in the Steam Cracking of Heptane at 700 °C (Gas Weight, % Mass)

flow of feed, g h ⁻¹	thiophene content, % mass		
	0.1	0.5	1.0
35.4	13.4	10.5	9.8
30.2	15.6	15.9	12.6
25.3	19.7	23.3	14.1
20.3	23.9	24.9	19.4
15.2	30.0	29.8	25.4

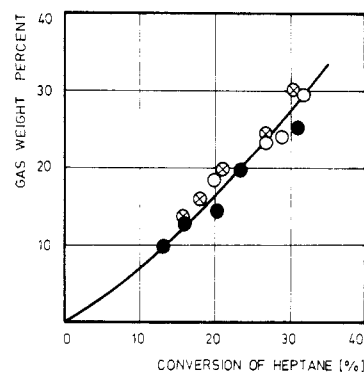


Figure 3. Gas production as a function of conversion of heptane at different thiophene contents (% mass): ⊗, 0.1; ○, 0.5; ●, 1.0.

experimental conditions (Bajus et al., 1979). The maximum deviation of the numerically calculated values in the presence of thiophene is 9.2%. Within the given interval of errors the values of the rate constants do not exhibit a decreasing nor an increasing trend as a function of the conversion. The presence of thiophene in the feed, in concentrations of 0.1 and 0.5%, increases the rate in comparison with the conversion of heptane without sulfur compound by 14%. A further increase of the level of thiophene in the reaction system has no longer a favorable effect on the rate of decomposition. The value of the rate constant at a concentration of 1% of thiophene is on the level of conversion of heptane itself. An equally favorable effect on the rate of thermal decomposition has also been found with elemental sulfur (Bajus and Veselý, 1980). Under comparable conditions the rate of conversion of heptane increased by as much as 28%.

Selectivity of Thermal Decomposition. The mean molecular mass of the gaseous conversion products from heptane is in the range 23.8–28.4. The amount of gaseous products grows with increasing conversion. Yields were determined with a standard deviation of less than 4.1%. Differences in yields at 0.1 and 0.5% concentrations of thiophene in the feed are negligible (Figure 3). At a concentration of 1% of thiophene, the measured yields are slightly, however significantly, lower. The yields of gaseous products as a function of the flow of heptane (Table II) show a similar dependence on the thiophene content.

The qualitative and quantitative composition of the liquid and gaseous product mixtures is given in Table III. The presence of thiophene has no influence on the qualitative composition. Among the products of the thermal

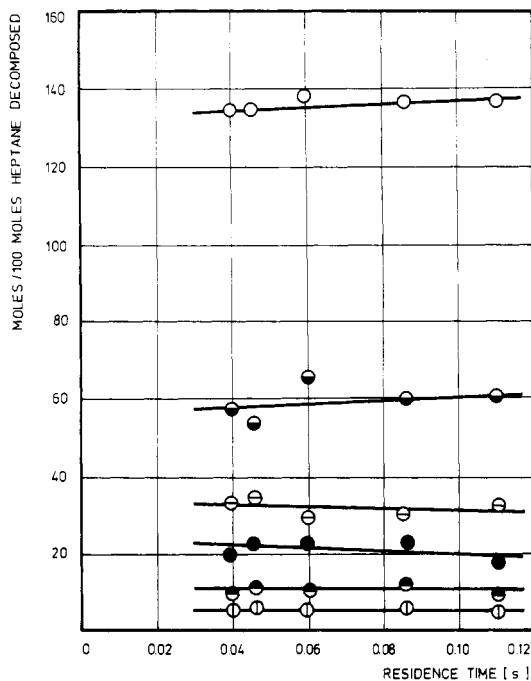


Figure 4. Product distribution vs. residence time for the conversion of heptane with 0.1% (mass) of thiophene: O, ethene; ●, methane; ⊖, propene; ●, 1-butene; ⊖, 1-pentene; ⊖, 1-hexene.

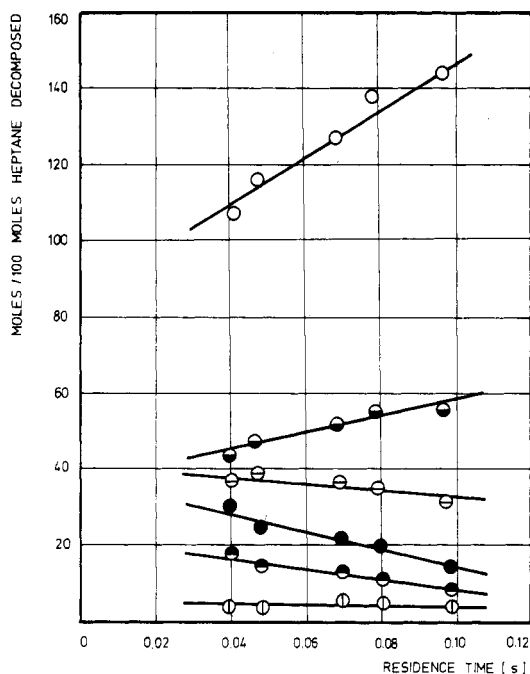


Figure 5. Product distribution vs. residence time for the conversion of heptane with 0.5% (mass) of thiophene: O, ethene; ●, methane; ⊖, propene; ●, 1-butene; ⊖, 1-pentene; ⊖, 1-hexene.

decomposition, ethene has a dominant position. From the remaining products the bulk is methane, propene, 1-butene, 1-pentene, 1-hexene, hydrogen, and carbon monoxide. Figures 4 to 6 show the effect of thiophene on the selectivity of the conversion of heptane as a function of the residence time. Thiophene only slightly influences the yields of propene, 1-butene, 1-pentene, and 1-hexene. In the case of methane, hydrogen, and carbon monoxide, the differences are greater and the course of their dependence on residence time is not unequivocal. Most obvious is the influence of thiophene on the selectivity of the conversion of heptane to ethene. Although in all experiments about 1.4 mol of ethene per mole of reacted heptane are formed, it is evident from Figures 4-6 that at a given thiophene

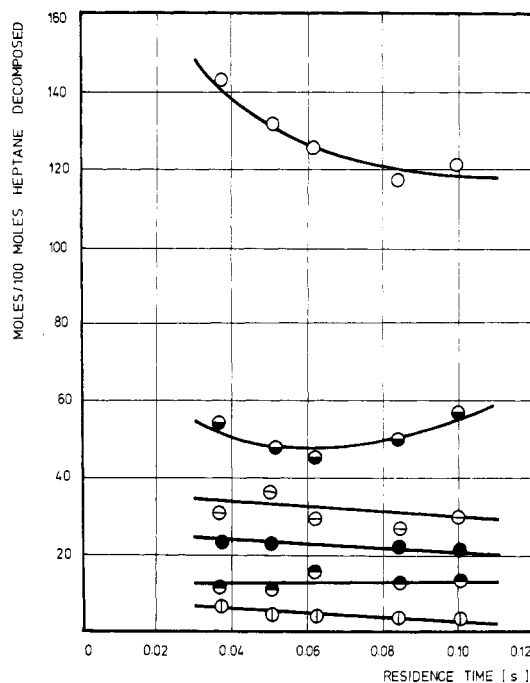


Figure 6. Product distribution vs. residence time for the conversion of heptane with 1.0% (mass) of thiophene: O, ethene; ●, methane; ⊖, propene; ●, 1-butene; ⊖, 1-pentene; ⊖, 1-hexene.

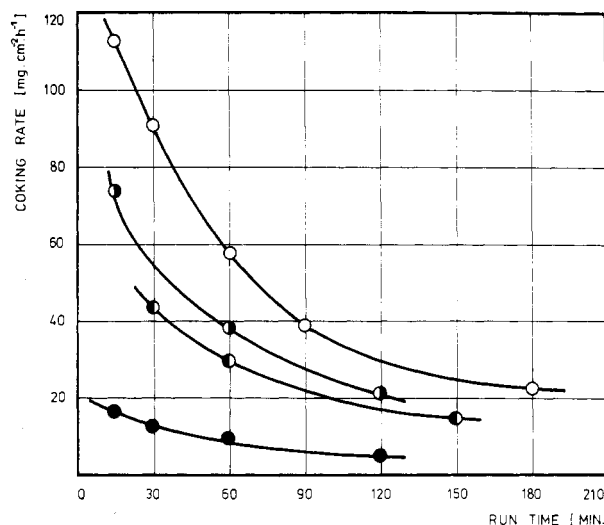


Figure 7. Rate of the formation of coke during the pyrolysis of reformer raffinate at different thiophene contents (% mass): O, without the inhibitor; ●, 0.05; ⊖, 0.1; ●, 0.5.

concentration the residence time is decisive. Within the range of observed residence times, the most uniform yields of ethene were obtained at 0.1% thiophene concentration. Selectivity toward ethene increases rapidly with increasing residence time at 0.5% concentration of thiophene. On the other hand, at 1% concentration of thiophene a slight decrease was observed.

Coking. The formation of coke was studied at 820 °C with reformer raffinate without thiophene and with 0.05, 0.1, and 0.5% (mass) of thiophene. The results are given in Table IV. The rate of coking as a function of the duration of the experiments is depicted in Figure 7. In the process the rate of coking is highest at the outset. After a certain time a steady state is reached. With increasing concentration of thiophene the rate of coking decreases. The course of coking indicates that at the beginning the influence of the inner surface is decisive on the course of reactions which lead to the formation of coke. The formation of coke is catalyzed by the metal surface. Only

Table III. Product Distribution in the Reaction Mixture from Steam Cracking of Heptane at 700 °C (mol/100 mol of Heptane Decomposed)

product	thiophene content, % mass							
	0 ^a	0 ^a	0.1	0.1	0.5	0.5	1.0	1.0
	conversion, %							
	13.88	26.80	15.60	21.00	14.30	32.06	13.19	31.03
	V _R , cm ³							
	4.84	6.85	5.47	5.94	5.64	5.94	5.10	6.11
	M.B., % mass							
	97.23	98.80	99.04	96.38	99.57	98.48	99.19	97.11
hydrogen	51.06	60.40	50.61	60.74	43.59	34.28	44.78	50.11
methane	49.52	66.87	58.19	66.76	43.59	54.40	54.02	50.68
ethane	6.18	10.01	10.43	8.90	9.59	15.97	11.06	8.55
ethene	116.65	137.75	135.51	140.17	106.64	143.50	143.63	122.66
propane	0.84	1.47	1.45	2.57	0.65	0.45	1.17	1.07
propene	31.90	38.24	33.61	28.82	36.65	32.53	30.14	30.28
butane	0.49	0.39	0.64	0.62	0.54	0.09	0.36	0.29
1-butene	21.30	20.24	19.62	23.01	30.24	14.52	22.26	21.26
<i>trans</i> -2-butene	0.42	0.33	0.28	0.22	0.31	0.02	0.07	0.27
<i>cis</i> -2-butene	0.26	0.37	0.23	0.22	0.25	0.19	0.07	0.22
1,3-butadiene	2.63	2.57	2.08	2.37	2.14	1.94	1.74	3.15
3-methylbutene	0.12	0.23	1.12	0.07	0.34	0.10	0.17	0.22
pentane	0.32	0.21	0.50	0.18	0.84	0.23	0.30	0.34
1-pentene	13.03	10.09	9.47	10.65	17.87	7.76	10.86	12.54
2-methyl-1-butene	0.35	0.19	0.11	0.12	0.32	0.17	0.07	0.29
<i>trans</i> -2-pentene	0.32	0.19	1.23	0.24	0.31	0.26	0.14	0.13
<i>cis</i> -2-pentene	0.25	0.22	0.20	0.08	0.13	0.13	0.18	0.10
1-hexene	6.0	5.52	5.09	5.10	3.18	4.17	5.39	5.76
1-heptene			2.10	1.18	2.57	0.25	5.13	1.84
carbon monoxide	26.19	12.44	26.78	26.71	19.65	17.95	11.88	32.84

^a The product distribution obtained in the absence of thiophene is taken from Bajus et al. (1979).

Table IV. Formation of Coke in the Pyrolysis of Reformer Raffinate at 820 °C and Residence Time 0.25 s

experiment duration, min	coke deposited, g	liquid products, g
Without Thiophene		
15	0.35	0.21
30	0.56	0.52
60	0.72	1.69
90	0.72	2.10
180	0.83	4.54
0.05% (Mass) Thiophene		
15	0.23	0.10
60	0.48	1.21
120	0.54	2.52
0.1% (Mass) Thiophene		
30	0.27	0.30
60	0.37	0.99
150	0.45	2.99
0.5% (Mass) Thiophene		
15	0.04	0.15
30	0.08	0.50
60	0.12	1.07
120	0.12	2.62

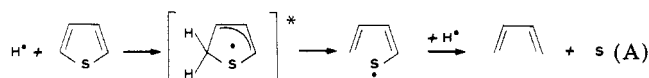
after a certain time, when the surface is covered by carbonaceous deposits, a steady state is reached. The presence of thiophene in the hydrocarbon feed causes an evident decrease in coking. As compared to the pyrolysis of the reformer raffinate without thiophene, the presence of 0.5% thiophene leads in steady-state conditions to an approximate sevenfold decrease in coke formation.

Discussion

The activation energy of decomposition of hydrocarbons is mainly determined by the dissociation energy of C-C bonds (297.3–347.5 kJ mol⁻¹), which split preferentially.

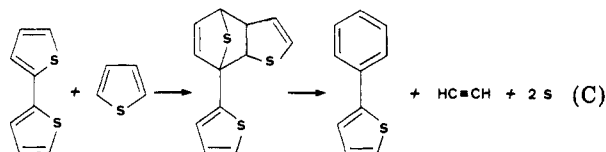
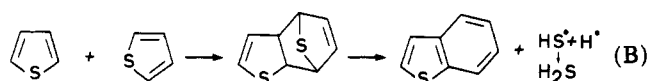
In the presence of aliphatic sulfur substances, the reaction can be initiated by the splitting of C-S bonds because the dissociation energy is in most cases less than 301.4–305.6 kJ mol⁻¹. However, it need not be so for thiophene, which is very similar in physical and chemical properties to benzene. *p*-Orbitals of double bonds and sulfur mutually cover up, giving rise to molecular wreath-shaped orbitals over and under the level of the nucleus. The resulting energy of stabilization by resonance is 129.8 kJ mol⁻¹ in thiophene and 163.3 kJ mol⁻¹ in benzene.

Comparison of kinetics, selectivity of decomposition, and rate of coking of heptane and of reformer raffinate leads to the finding that thiophene influences the radical conversion in the homogeneous phase and the surface reactions in the reactor. Under the given experimental conditions reactions can occur between thiophene molecules themselves and between thiophene and the highly reactive radicals resulting from the decomposition of hydrocarbons, e.g. H· and R·. Decomposition of thiophene in the presence of hydrogen at 25–425 °C under lower pressures (725 Pa) is, according to Horie et al. (1975), very selective. Among the products, no sulfur compound was found except hydrogen sulfide. On this basis it is possible to postulate that reaction A is initiated on C-2 of thiophene, which also is the most reactive position for electrophilic substitution. This gives rise to a radical which, while opening the ring, decomposes to a thiobutadienyl radical, which further reacts with a hydrogen radical to butadiene and a sulfur atom.

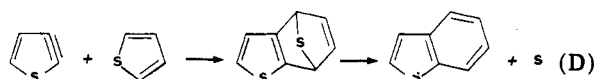


Wynberg and Bantjes (1959) pyrolyzed thiophene at 800–850 °C. Among the reaction products, bithienyl as well as benzothiophene and phenylthiophene was found. The formation of these products was explained by Diels-

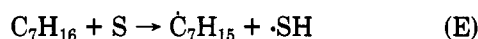
Alder addition of thiophene itself according to reactions B and C.



Fields and Meyerson (1967) ascribe a very important role to thiophyne, which can be formed by intramolecular dehydrogenation of thiophene, as a reactive intermediate product. Reaction with a thiophene molecule could give benzothiophene according to reaction D.

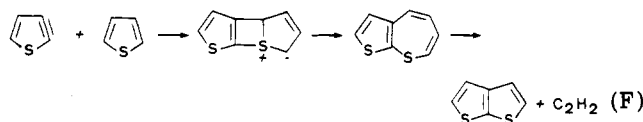


From the proposed mechanisms for the thermal conversion of thiophene, the release of sulfur (reactions A, C, and D) and hydrogen sulfide (reaction B) is characteristic. Sulfur eliminated from thiophene can enter into reactions in the gaseous state. It can also react with the metal surface of the reactor, similarly as in the case of aliphatic sulfur substances. From the possible reactions, sulfur can initiate propagation according to reaction E with the formation of heptyl and $\cdot\text{SH}$ radicals.

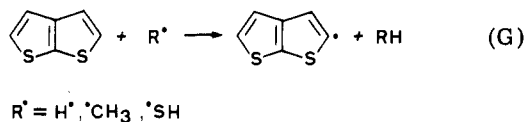


The observed increase in the rate of decomposition of heptane evidently shows that the course according to reaction E is preferred whenever the level of thiophene in the reaction system is low (less than 0.5% mass per feed).

When the concentration of thiophene is increased, addition reactions can take place, where neither sulfur nor $\cdot\text{SH}$ radicals are released. An example is the 1,2 addition of thiophene with its intermediate reaction product thiophyne (reaction F), yielding thiophthene and acetylene (Fields and Meyerson, 1967).



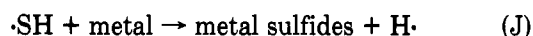
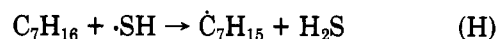
Thiophthene can react with highly active radicals (reaction G).



In this propagation relatively less active 2-thiophthenyl radicals are formed. Benzothiophene can react similarly as thiophthene.

Thus, at higher thiophene concentrations, a state is reached where either thiophene or its decomposition products behave similarly as unsaturated hydrocarbons or aromatics. These compounds act as scavengers of active radicals from hydrocarbon decomposition, and the rate of thermal decomposition decreases.

Radicals $\cdot\text{SH}$ from reactions B and E can also cause propagation according to reaction H, termination according to reaction I, or react with the surface of stainless steel to metal sulfides according to reaction J.



The presence of metal sulfides was verified by the analysis of the carbonaceous deposits from the reactor. For example, after passivation by hydrogen sulfide, 25.5% (mass) of metal sulfides were formed, from which 36.4% (mass) were chrome sulfides and 22.5% (mass) iron sulfides (unpublished results). The small layer of metal sulfides which can be formed according to reaction J slows the course of secondary reactions leading to coke.

Conclusions

Thiophene introduced into the reaction system together with the starting hydrocarbon influences the decomposition rate, selectivity, and coke formation in the pyrolysis of hydrocarbons. The extent of these effects is dependent largely on the concentration of the sulfur compound. In the steam cracking of heptane, in the presence of 0.1 and 0.5% mass of thiophene, the rate of decomposition increases by about 14% in comparison with the conversion in the absence of thiophene. A further increase of the concentration of thiophene to 1.0% mass decreases the rate of decomposition of heptane to the level of the conversion of the pure hydrocarbon itself.

When heated in the presence of thiophene, the formation of coke is inhibited considerably, mainly as a result of passivation of the inner surface of the reactor. The rate of coking is inversely proportional to the content of thiophene in the reformer raffinate. The protective layer is composed of metal sulfides which are probably formed by the reaction of $\cdot\text{SH}$ radicals or S atoms with the wall of the reactor.

Nomenclature

S = inner surface of the reactor, cm^2

V = reactor volume, cm^3

k = first-order rate constant, s^{-1}

x = conversion of heptane

V_R = equivalent reactor volume, cm^3

r_c = coking rate, $\text{mg cm}^{-2} \text{h}^{-1}$

M.B. = material balance of the hydrocarbon part

Greek Letters

ν = moles of product formed per mole of heptane decomposed

ϵ = relative volume change in the reactor

τ = residence time, s

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