

The results of the current study support the view that the principal role of  $\text{CO}_2$  is to maintain the catalyst in an active state rather than to take place in a direct hydrogenation to methanol.

### Conclusions

This study has demonstrated that novel catalysts of the Raney type, produced by the caustic extraction of aluminum-copper-zinc alloys shows high activity and selectivity for methanol synthesis. The main factors which affect the ability of these catalysts to produce methanol are the composition of the starting alloys and the extraction procedures used to leach the aluminum and some of the zinc from the alloy.

While the composition of the final catalyst was found to be a function of both the initial alloy composition and the extraction conditions, an alloy composition range for optimal methanol synthesis catalysts was found to be 33-43 wt % copper, 7-17 wt % zinc and 50% aluminum. Conditions of extraction were found to have marked influence on selectivity. In general, catalysts prepared under more severe the conditions exhibit higher selectivity and activity for methanol synthesis.

It is apparent that considerably more research is required into these catalysts, first into the quite complex area of alloy extraction and secondly into their industrial applicability with regard to poisoning and thermal stability,

two properties which have caused problems in other copper-based methanol synthesis catalysts (Dewing and Davis, 1975).

### Literature Cited

- Casey, T. D.; Chapman, G. M. (to Catalysts and Chemicals, Inc.), U.S. Patent 3 790 505, Feb 5, 1974.  
 Chang, C. D.; Silvestri, A. J. (to Mobile Oil Corporation), U.S. Patent 3 894 102, June 1975.  
 Davies, P.; Snowdon, F. E. (to Imperial Chemical Industries Ltd.), U.S. Patent 3 326 956, June 20, 1967.  
 Dewing, J.; Davis, D. S. *Adv. Catal.* **1975**, *24*, 221.  
 Freil, J.; Pieters, W. J. M.; Anderson, R. B. *J. Catal.* **1969**, *14*, 247.  
 Haynes, W. "American Chemical Industry—A History, Vol. IV 1923-29"; Von Nostrand Co.; Amsterdam, 1948; p 169.  
 Herman, R. G.; Klier, K.; Simmons, G. W.; Finn, B. P.; Bulko, J. B.; Kobylinski, T. P. **1979**, *J. Catal.* **1979**, *56*, 407.  
 Humphreys, G. C.; Ashman, D. J.; Harris, N. *Chem. Econ. Eng. Rev.* **1974**, *6*, 26.  
 Nadirov, N. K.; Ashirov, A. M.; Savel'ev, A. F.; Zhushupova, A. *Z. Fiz. Khim.* **1977**, *51*, 1422.  
 Schermuly, O.; Luft, G. *Chem. Ing. Techn.* **1977**, *49*, 11.  
 Supp, E., *Chem. Tech.*, *3*, 430 (1973).  
 Voltz, S. E.; Wise, J. J. "Development Studies on Conversion of Methanol and Related Oxygenates to Gasoline", 1976, Final Report, ERDA ERDA E(49-18)-1773.  
 Zahner, J. C. (to Mobil Oil Corp.), U.S. Patent 4 011 275, Mar 8, 1977.

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## Steam Cracking of Hydrocarbons. 3. Straight-Run Naphtha

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Steam cracking of straight-run naphtha from Romashkino crude oil was investigated in quartz and stainless steel reactors with a relatively large ratio of inner surface to volume. The experiments were performed at atmospheric pressure at 780-800 °C for starting ratios of steam to naphtha between 0.5 and 1.0, with residence times of 0.1-0.4 s. The influence of the reactor material, the temperature, the ratio of steam to hydrocarbon, the residence time, and the presence of sulfur compounds is discussed in terms of coke formation and yields of various reaction products. The reaction products were analyzed by gas chromatography, using packed columns for the analysis of the gaseous products and capillary columns for the liquid products. About 200 compounds were identified in the liquid mixture. Reference standard hydrocarbons, published retention data, and mass spectrometry were used for the identification.

### Introduction

In the pyrolysis of individual hydrocarbons and petroleum fractions to desired olefins, not only primary reactions but also secondary reactions occur. Many products of splitting, dehydrogenation, hydrogenation, and condensation reactions are formed. The composition of the product mixture is influenced by the reaction conditions. Important factors are also the type of reactor, the properties of the construction material, the ratio of inner surface to volume, and the activation or passivation of the inner surface of the reactor by chemical compounds. The pyrolysis of ethane (Dunkleman and Albright, 1976a;

Brown and Albright, 1976), propane (Brown and Albright, 1976; Crynes and Albright, 1969; Tamai and Nishiyama, 1970; Dunkleman and Albright, 1976b), butanes (Hurd and Pilgrim, 1933), heptane (Melikadze et al., 1975; Bajus et al., 1979a), methylcyclohexane (Bajus et al., 1979b), ethene (Brown and Albright, 1976; Hurd and Eilers, 1934), propene (Hurd and Eilers, 1934; Ghaley and Crynes, 1976), methylpropene and its dimers, and 2-pentene (Hurd and Eilers, 1934) has been investigated. Nonmetallic materials (glass, quartz, porcelain), metals (iron, nickel, gold, silver, cobalt, titanium), alloys (monel, incoloy, incoloy 800), and stainless steel of different compositions were used as re-

actor materials in these studies.

The properties of a reaction system, consisting of a stainless steel reactor with relatively large inner surface, were investigated in the steam cracking of heptane (Bajus et al., 1979a) and methylcyclohexane (Bajus et al., 1979b). In this system the thermal decomposition of  $C_7$  hydrocarbons proceeded with a relatively low activation energy of about  $200 \text{ kJ mol}^{-1}$ . The influence of the inner surface on the selectivity of the conversion was reflected in a reduced yield of methane and ethane. Since high molecular products and coke were absent, it was supposed that either they are not formed or, more probably, they reacted under the influence of the reactor wall with steam to produce carbon monoxide and hydrogen.

The presence of sulfur compounds is supposed to cause passivation of the inner surface as a consequence of the formation of a sulfide protection film. It has been shown that the continuous dosage of elemental sulfur together with the hydrocarbon feed influences the rate and the selectivity of the conversion and the formation of coke, whereby these effects depend to a large extent on the properties of the surface (Bajus and Veselý, 1979).

Proceeding from the above results, we investigated the steam cracking of straight-run naphtha in stainless steel and quartz reactors. The influence of the reactor material, the temperature, the feed ratio of steam to hydrocarbon, the residence time, and the presence of sulfur compounds on the yields of various reaction products is discussed in this paper. A substantial part of this work was devoted to the separation and identification of the liquid reaction products.

## Materials and Methods

The straight-run naphtha originated from Romashkino crude oil. Its composition, expressed as % mass, was unbranched alkanes, 37.2; branched alkanes, 44.8; cycloalkanes, 13.9; aromatic hydrocarbons, 3.1. The density was  $668 \text{ kg/m}^3$ , the molecular mass 86.2, and the distillation range  $34\text{--}125^\circ\text{C}$ . The sulfur content was 0.016% (mass).

The equipment was described earlier (Bajus et al., 1979a). The tubular flow reactors were made from stainless steel and quartz. The ratio of inner surface to volume of the reactor was  $6.65 \text{ cm}^{-1}$  for stainless steel and  $4.82 \text{ cm}^{-1}$  for quartz. Constant reaction conditions were secured by decreasing the partial pressure of the reactants and by passivation of the inner surface of the reactor wall. Steam was used as diluent, while the sulfur compounds, present in the straight-run naphtha, act as surface-active agents. In this way maximum reproducibility of the cracking process was attained, and the equipment could work continuously.

The temperature was monitored along the reactor. From the longitudinal temperature profile measurements, the equivalent volume of the reactor was calculated according to Hougen and Watson (1947). This equivalent volume was used for the calculation of the residence times (Bajus et al., 1979a).

The straight-run naphtha feed was varied between 0.04 and  $0.58 \text{ mol h}^{-1}$  and that of distilled water between 1.08 and  $2.78 \text{ mol h}^{-1}$ . The weight ratio of water to straight-run naphtha was 0.5 to 1.0.

Gas-chromatographic analysis of the gaseous and liquid products was performed in the same way as reported previously (Bajus et al., 1979a,b). Gaseous products were analyzed on columns packed with ethylene glycol dibutylate (1,2-ethanediol dibutanoate) on Chromosorb P. Ethane and ethene were separated on Florisil, and hydrogen and carbon oxides on Supersorb. Liquid products were analyzed on a  $100 \text{ m} \times 0.25 \text{ mm}$  i.d. capillary column,

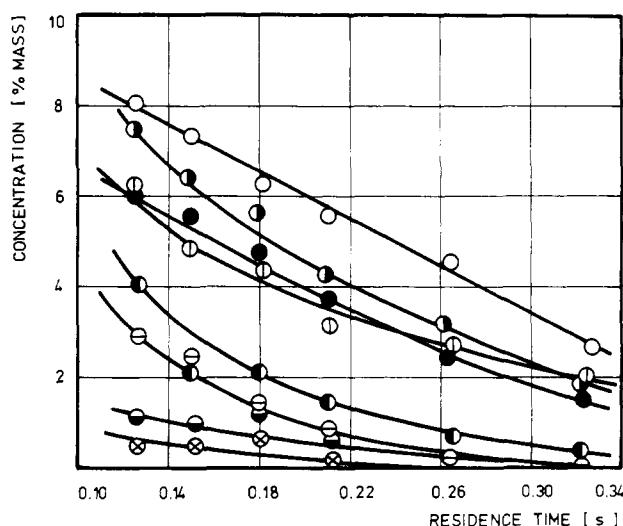


Figure 1. Effect of the residence time on the concentration of alkanes in the liquid product mixture from the steam cracking of straight-run naphtha in a stainless steel reactor at  $780^\circ\text{C}$ : (○) pentane; (◇) methylbutane; (●) hexane; (◐) isohexanes; (◑) heptane; (◒) isooheptanes; (△) octane; (◔) isooctanes.

coated with squalane. The same column was used in GC/MS analysis (Leferink and Leclercq, 1974). The retention indexes were determined with a precision corresponding to a standard deviation of less than 0.5 index units. In some instances, the differences between measured and tabulated data are somewhat larger because of incomplete separation, the effect of the nature of the carrier gas, and mean column pressure, etc.

The yields of gaseous and liquid products and the concentration of the components in the product mixture were determined with a standard deviation of less than 5%. The total material balance of hydrocarbons and water varied between 95 and 100%, and that of hydrocarbons only between 95 and 105%. No measurements were taken to indicate quantities of carbon formed.

## Results

The conversion of straight-run naphtha depends mainly on the reactor temperature and the residence time. At longer residence times and higher temperatures, increased yields of unsaturated hydrocarbons and methane are obtained. These products originate mainly from alkanes, as these represent 82% of the straight-run naphtha feed. The favorable influence of the increase in residence time on the conversion of straight-run naphtha is reflected by a decreased concentration of alkanes in the final products (Figure 1). Table I shows the different concentrations of individual alkanes in the product mixture from a stainless steel reactor, expressed as the ratio of the respective hydrocarbon in the feed and in the product. At long residence times, this ratio increases with molecular mass from butanes to heptanes. The conversion of 2-methylhexane and 3-methylhexane is even higher than that of heptane. The conversion of octanes is relatively lower. These results are in agreement with those obtained under comparable conditions from individual unbranched alkanes  $C_5\text{--}C_{12}$  (Bajus and Veselý, 1976), where heptane showed the highest conversion, as well as the highest yield of ethene. Predictably, branched alkanes are converted to a higher degree because a reactive tertiary carbon atom is present in the chain.

The composition of the product mixture from the steam cracking of straight-run naphtha in stainless steel and quartz reactors is shown in Table II. The yields of gaseous products vary from 65.2 to 93%. As expected, the gaseous

Table I. Conversion of Alkanes in the Steam Cracking of Naphtha at 780 °C<sup>a</sup>

alkane	residence time, s		
	0.21	0.26	0.32
methylpropane	4.5	3.8	3.1
butane	3.3	3.3	4.2
methylbutane	5.1	3.6	8.1
pentane	4.5	4.6	8.0
2-methylpentane	5.0	6.1	11.0
3-methylpentane	3.6	5.0	11.7
hexane	3.0	4.7	7.1
2-methylhexane	5.7	16.1	25.3
3-methylhexane	5.6	16.7	31.4
heptane	3.9	12.3	19.4
2-methylheptane	2.6	9.0	11.3
octane	3.2	4.5	13.5
3-ethylhexane + 3-methylheptane	4.9	7.8	13.0

<sup>a</sup> Ratio of concentrations (% mass) of corresponding alkanes in the feed and in the product mixture.

fraction increases with temperature and residence time. The qualitative composition of the product mixture from both types of reactors is the same.

The main product at the given conditions is ethene. Further dominating olefins are propene, methylpropene, 1-butene, and 1,3-butadiene. Among the low molecular alkanes, methane predominates. At increasing residence times, yields of these products are increasing. The yields of ethene and other products from both reactors are comparable, except for methane and ethane. The effect of the residence time on the formation of ethene, methane, and ethane is shown in Figure 2. Apparently the quality of the reactor wall has a significant influence on the thermal conversion of hydrocarbons present in straight-run naphtha. The formation of methane and ethane in stainless steel is, all other conditions being equal, lower than in quartz. The same wall effect was observed with heptane

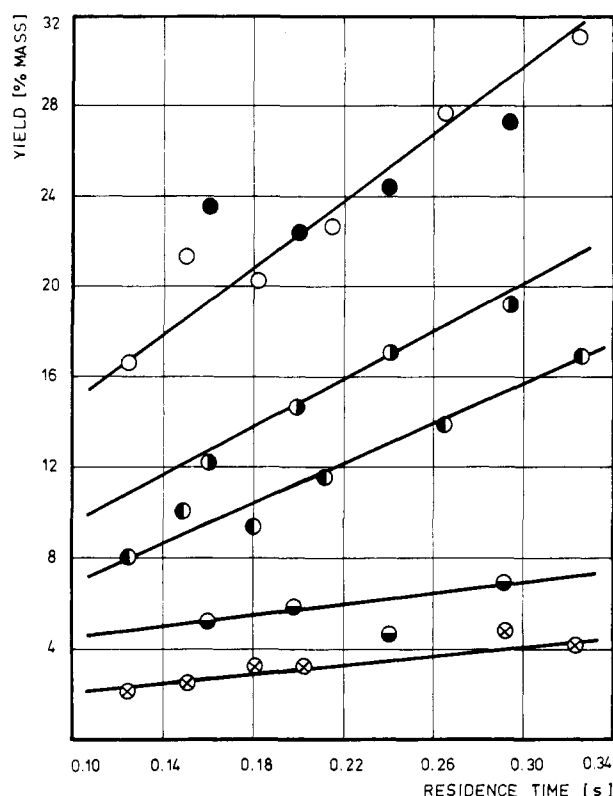


Figure 2. Product distribution vs. residence time for the steam cracking of straight-run naphtha. In a stainless steel reactor: (○) ethene; (●) methane; (⊗) ethane. In a quartz reactor: (●) ethene; (●) methane; (⊗) ethane.

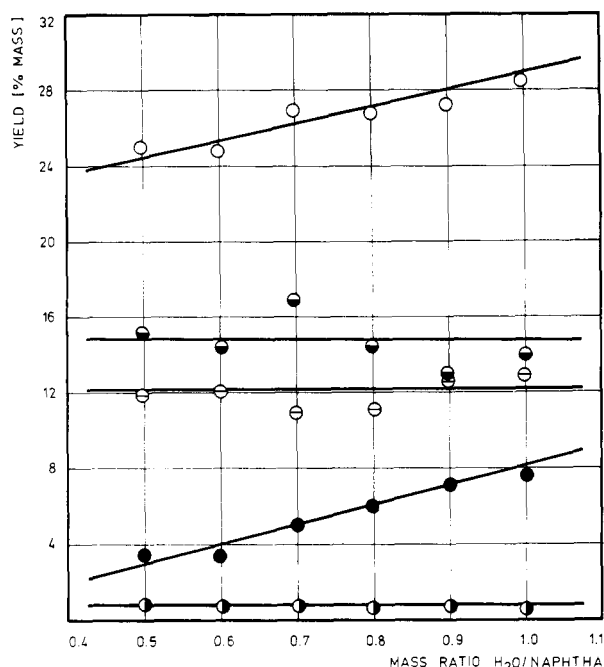
(Bajus et al., 1979a) and methylcyclohexane (Bajus et al., 1979b) in a reactor with a high ratio of surface to volume.

Another characteristic feature of the wall is its influence on the composition of the liquid product mixture. The

Table II. Composition of the Gaseous Product Mixture (% Mass) from the Steam Cracking of Naphtha<sup>a</sup>

hydrocarbon	reactor material							
	stainless steel						quartz	
	temp, °C							
	780	780	780	800	800	800	780	780
	residence time, s							
	0.12	0.21	0.32	0.12	0.21	0.32	0.20	0.29
methane	8.47	11.67	17.03	11.94	14.61	20.11	14.82	19.39
ethane	2.14	3.33	4.26	2.91	3.28	4.68	5.79	6.98
ethene	16.69	22.64	31.29	26.75	29.09	36.78	22.68	27.35
propane	1.08	0.95	0.40	1.02	0.97	0.50	2.06	0.66
propene	11.15	18.37	19.24	13.51	17.00	14.09	17.54	19.78
methylpropane	0.23	0.18	0.15	0.21	0.14	0.07	0.10	0.13
butane	1.48	1.01	0.81	1.48	0.76	0.24	0.11	0.79
methylpropene; 1-butene	4.99	6.42	5.70	5.79	4.97	3.32	6.15	2.71
trans-2-butene	0.57	0.80	0.67	0.60	0.54	0.60	0.65	0.24
cis-2-butene	0.43	0.35	0.49	0.30	0.55	0.88	0.37	0.46
methylbutane	4.06	2.96	1.95	3.74	2.03	0.74	2.35	1.84
1,3-butadiene	2.20	3.01	4.40	3.80	4.37	4.01	2.70	4.08
3-methyl-1-butene	0.18	0.05	0.06	0.11	0.10	0.10	0.09	0.07
pentane	4.21	3.92	2.46	4.43	2.74	0.73	3.21	2.36
1-pentene	0.28	0.31	0.15	0.26	0.17	0.04	0.17	0.16
2-methyl-1-butene	0.28	0.35	0.19	0.36	0.30	0.08	0.21	0.18
cis-2-pentene	0.36	0.08	0.08	0.15	0.25	0.15	0.22	0.13
3-methyl-1-butene	0.10	0.03	0.06	0.22	0.05			0.03
2-methylpentane	2.24	1.43	0.92	1.39	0.78	0.37	0.87	0.46
pentadiene	0.09	0.46	0.80	0.69	0.75	0.11	0.06	0.16
3-methylpentane	1.46	0.92	0.38	0.95	0.55	0.33	0.37	0.20
hexane	2.50	2.27	1.26	1.83	1.08	0.20	0.99	0.55
other hydrocarbons (>C <sub>6</sub> )			0.27	0.16	0.23	0.26		
total	65.19	82.45	93.04	82.25	85.27	88.30	83.72	88.72

<sup>a</sup> Mass ratio of water to feed 0.5:1.



**Figure 3.** Effect of steam on the conversion of straight-run naphtha at 780 °C and a residence time of 0.18 s in a stainless steel reactor: (O) ethene; (◐) propene; (◑) methane; (●) carbon monoxide; (◑) hydrogen.

liquid residue from the quartz reactor is a dark-brown, high-boiling mixture with aromatic character. Typical compounds are substituted biphenyls and polyaromatic hydrocarbons. Their separation and identification will be reported in part 4 of this series.

The liquid products (Table III) of straight-run naphtha from a stainless steel reactor are transparent, lightly colored, and of relatively low boiling range. The products have been separated at two temperatures and identified by matching measured retention data with those published by Rijks and Cramers (1974), Loewenguth and Tourres (1968), Soják and Rijks (1976), Hively and Hinton (1968), and Tourres (1967) and by mass spectrometry. The chromatograms of the analyzed samples showed about 200 peaks. All but 13 components were identified. According to their origin the products fall into two groups. The first group contains nonconverted alkanes, cycloalkanes, and aromatic hydrocarbons from the feed. The second group, which predominates, includes alkenes, alkadienes, cycloalkenes, and aromatic hydrocarbons. The liquid does not contain naphthalene nor its monomethyl and dimethyl homologues, fluorene, phenanthrene, anthracene, and biphenyl, which are the main components in the fraction boiling over 180–200 °C, the so-called pyrolytic oil, as found with quartz reactors.

The absence of the pyrolytic oil and of higher-boiling aromatic hydrocarbons on one side and the presence of carbon oxides, especially carbon monoxide, on the other side has given rise to a more detailed study of the influence of steam in the conversion of straight-run naphtha in a stainless steel reactor. The mass ratio of steam to hydrocarbon feed was varied from 0.5 to 1.0. The flows of feed and of water were chosen in such a way that the residence time was maintained at 0.18 s. An increase of the mass ratio water/naphtha, in the given interval, increases the yield of gaseous products from 81.2 to 89.5%. The influence of this ratio on the yields of ethene, propene, methane, carbon monoxide, and hydrogen is shown in Figure 3. The yield of ethene increases from 25.1 to 28.7% (mass). Apparently, the decrease of the partial pressure

of the reacting components does not have a significant effect on the formation of methane and propene. Further gaseous olefins, which are present in larger amounts among the products, are methylpropene and 1-butene (cf. Table II). Their yield is about 5% (mass). The yield of 1,3-butadiene increases from 3.9 to 5.0% (mass). An increase in the steam-to-naphtha ratio enhances the formation of carbon monoxide. Its content increases from 3.3 to 7.6% (mass). The yield of hydrogen varies between 0.51 and 0.83% (mass). Among the liquid products there is an increase in the concentrations of benzene, toluene, styrene, and other C<sub>8</sub>–C<sub>11</sub> aromatics, at increasing steam-to-naphtha mass ratio.

### Discussion

In the steam cracking of straight-run naphtha, the most reactive components are C<sub>6</sub>–C<sub>8</sub> alkanes. The conversion of branched alkanes is higher than that of unbranched alkanes. The presence of tertiary carbon atoms facilitates the formation of initiating radicals. The composition of the reaction product mixtures leads to the supposition that not only C–C bonds but also C–H bonds are split. For example 3-methylhexane, the most reactive heptane, might yield a hexyl radical by splitting off a methyl radical, or a heptyl radical by splitting off a hydrogen radical at the tertiary carbon atom. According to the Rice theory, these radicals yield 1-pentene, 2-hexene, 3-hexene, 1-butene, 2-methyl-1-butene, 2-methyl-1-pentene, 3-methyl-3-hexene, and 3-methyl-2-hexene, and in addition methyl, ethyl, and hydrogen radicals. All mentioned olefinic products have been identified. In the same way the products from the splitting of other hydrocarbons in the feed can be derived.

The composition of the product mixtures shows that, besides primary splitting reactions, secondary reactions occur. They are influenced by reaction conditions (temperature, residence time, partial pressure) and to a substantial extent also by the ratio of diluent to feed, the quality of the wall, the ratio of inner surface to reactor volume, and, last but not least, by the activation or passivation of the inner surface.

The effect of the surface of the reactor is treated in most papers only from the standpoint of initiation and termination of radicals. The surface, however, has a decisive influence on the rate and on the course of secondary reactions. It must be considered that the behavior of the inner surface is determined not only by the reactor material but also by the composition of the feed and the influence of steam. In secondary reactions carbon is formed, which is deposited as coke on the reactor wall. In a stainless steel reactor with relatively large surface, the formation of coke is substantially lower in the steam cracking of straight-run naphthas than of individual hydrocarbons (Bajus et al., 1979a,b; Bajus and Veselý, 1976) or gasoline from catalytic reforming after the extraction of aromatic hydrocarbons. These differences are due to different contents of sulfur compounds in the feeds. The straight-run naphtha contained 0.016% (mass) of sulfur, while the other feeds mentioned were practically free of sulfur. It has been found that the formation of coke is inhibited by the addition of elemental sulfur to the latter feeds (Bajus and Veselý, 1979).

The inhibition of coke formation by sulfur compounds could be rationalized as the following. During the cracking, intermediate HS· radicals could be formed from sulfur compounds, e.g., from mercaptans. These radicals might be partly converted to hydrogen sulfide by reaction with hydrocarbons. Partly they enter into the reaction with the heterogeneous phase according to reaction 1 with formation

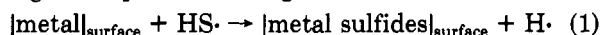


Table III. Retention Indexes of Steam Cracking Products from Naphtha on a Capillary Squalane Column<sup>a</sup>

	<i>I</i> <sub>50</sub>		<i>I</i> <sub>70</sub>		confirmation by MS
	measd	RC <sup>f</sup>	measd	RC <sup>f</sup>	
methane					
ethane; ethene					
propene					
propane					
methylpropene					
1-butene; 1,3-butadiene					
butane					
<i>trans</i> -2-butene	407.1	406.6	405.7	406.3	
<i>cis</i> -2-butene	416.9	416.9	416.4	417.3	
1,2-butadiene	429.5	430.4 <sup>c</sup>	428.6	430.3 <sup>c</sup>	
3-methyl-1-butene	450.5	450.3	449.8	450.8	
2-methyl-1-butene-3-yne	456.0	456.8 <sup>c</sup>	455.0	456.9 <sup>c</sup>	
1,4-pentadiene	461.7	461.7 <sup>b</sup>	462.5	462.6 <sup>b</sup>	
methylbutane	474.0	475.3	474.8	475.5	
1, <i>trans</i> -2-dimethylcyclopropane	477.1	479.2			
1-pentene	480.8	481.8	481.5	482.1	
2-methyl-1-butene	487.2	488.0	487.8	488.1	
pentane					
<i>cis</i> -2-pentene	504.8	504.9	505.5	505.1	
1, <i>trans</i> -3-pentadiene	514.8	515.8	516.4	516.5	
1,3-cyclopentadiene	520.3	521.7 <sup>c</sup>			
1, <i>cis</i> -3-pentadiene	523.9	524.2 <sup>b</sup>	524.1	525.1 <sup>b</sup>	
2,3-pentadiene	529.3	530.2	531.5	529.5	
3-methyl-1,4-pentadiene	532.6	532.3 <sup>c</sup>			
2,2-dimethylbutane	538.2	536.8	538.3	538.5	
unidentified	543.2		544.1		
4-methyl-1-pentene	548.5	549.4	551.7	550.4	
cyclopentene	550.3	549.5			
3-methyl-1-pentene	552.5	551.4			
4-methyl- <i>cis</i> -2-pentene	557.1	556.2	556.7	556.6	
2,3-dimethyl-1-butene	559.5	558.8	559.5	559.6	
1,5-hexadiene	563.3	562.9	563.4	563.7	
cyclopentane	566.1	565.7	568.1	568.5	
2,3-dimethylbutane	567.8	567.3			
2-methylpentane	570.1	569.7	569.9	570.0	
2-methyl-1-pentene	580.1	580.1	580.6	580.6	
1-hexene	582.2	582.3	582.6	582.7	
3-methylpentane	584.3	584.2	585.0	585.1	
1, <i>cis</i> -4-hexadiene	587.1	586.9 <sup>b</sup>	588.3	587.8 <sup>b</sup>	
unidentified	589.4				
<i>cis</i> -3-hexene	592.0	592.6	591.9	593.0	
<i>trans</i> -2-hexene	596.9	596.9	596.9	596.7	
2-methyl-2-pentene	597.7	597.8			
hexane					
3-methyl- <i>cis</i> -2-pentene	602.9	602.8	604.3	603.4	
4,4-dimethyl-1-pentene	606.1	604.6	606.0	606.5	
2,3-dimethyl-1,3-butadiene	610.4	610.9 <sup>c</sup>	611.2	612.8 <sup>c</sup>	
3-methyl- <i>trans</i> -2-pentene	612.3	612.7	612.9	612.9	
unidentified	622.3		625.5		
2-methyl-1,3-cyclopentadiene	624.2	623.9 <sup>b</sup>	627.3	627.9 <sup>b</sup>	
methylcyclopentane	627.4	627.9	628.9	631.0	
2,4-dimethylpentane	529.5	529.8	631.0	630.5	
4,4-dimethyl- <i>cis</i> -2-pentene	635.8	635.5	637.5	637.6	
benzene	637.4	637.2 <sup>d</sup>	642.6	642.0 <sup>d</sup>	
3-methyl-1, <i>trans</i> -3-pentadiene	640.7	640.7 <sup>b</sup>			
1-methylcyclopentene	644.0	644.0	646.6	646.8	
2,3-dimethyl-1-pentene	650.0	650.4	650.7	652.2	
5-methyl-1-hexene	651.4	650.6 <sup>c</sup>	653.2	652.2 <sup>c</sup>	
1,3-cyclohexadiene	652.3	654.7 <sup>c</sup>	655.0	659.4 <sup>c</sup>	
4-methyl- <i>trans</i> -2-hexene	657.2	656.7	657.3	657.4	
4-methyl-1-hexene	658.6	657.9	660.7	659.3	
5-methyl- <i>trans</i> -2-hexene	659.8	659.5			
cyclohexane	662.3	662.7	664.5	667.2	
2-methylhexane	666.5	666.6	666.9	667.0	
3,4-dimethyl- <i>cis</i> -2-pentene	669.3	670.6	670.4	671.5	
2,3-dimethylpentane	671.4	671.7	673.2	673.4	
1,1-dimethylcyclopentane	673.0	673.5	675.4	677.1	
3-methylhexane	676.1	676.2	676.8	676.9	
2-methyl-1-hexene	677.9	678.1	678.7	678.5	
3,4-dimethyl- <i>trans</i> -2-pentene	679.1	679.0 <sup>c</sup>	680.3	679.5 <sup>c</sup>	
1-heptene	682.3	681.8	682.2	682.3	
3-methyl- <i>cis</i> -3-hexene			684.1	685.0	
1, <i>cis</i> -3-dimethylcyclopentane			685.6	685.9	
3-ethylpentane	686.3	686.0	686.9	687.2	
1, <i>trans</i> -2-dimethylcyclopentane	688.9	689.2	692.4	692.4	
<i>cis</i> -3-heptene	690.5	690.4	689.8	691.1	

Table III (Continued)

	$I_{50}$		$I_{70}$		confirmation by MS
	measd	RC <sup>f</sup>	measd	RC <sup>f</sup>	
3-methyl- <i>cis</i> -2-hexene	692.9	693.3	695.4	694.1	
3-ethyl-2-pentene	696.9	697.2			
<i>trans</i> -2-heptene	698.4	698.4	698.2	698.5	
heptane					
2,3-dimethyl-2-pentene	702.7	703.4	703.6	704.2	
2,4,4-trimethyl-2-pentene	704.0	704.3	704.9	706.8	
unidentified	705.2		706.8		
unidentified	707.9		708.3		
unidentified	711.8		711.6		
3-ethylcyclopentene	713.2	712.4	715.7	715.8	
2,2-dimethyl- <i>cis</i> -3-hexene	716.1	716.8	716.8	718.8	
2,2-dimethylhexane	719.5	719.4	720.2	720.5	
1, <i>cis</i> -2-dimethylcyclopentane	720.5	720.9	724.9	725.1	
3-heptyne	722.3	721.6 <sup>c</sup>	721.9	720.4 <sup>c</sup>	
1,1,3-trimethylcyclopentane	723.5	723.6	727.3	727.5	
methylcyclohexane	725.5	725.8	730.7	730.6	
2,5-dimethylhexane	728.4	728.4	728.9	729.0	
3-methylcyclohexene	730.5	730.7 <sup>b</sup>	735.5	735.7 <sup>b</sup>	
3,4-dimethylhexane	731.9	731.9	732.8	732.8	
4-methylcyclohexene	732.8	733.1 <sup>b</sup>			
ethylcyclopentane	733.5	733.8	737.5	737.5	
2,2,3-trimethylpentane	736.7	737.1	741.0	740.2	
2,3-dimethyl-1-hexene	738.9	739.3			
1, <i>trans</i> -2, <i>cis</i> -4-trimethylcyclopentane	740.8	741.1	744.3	744.5	
3,3-dimethylhexane	743.0	743.5	746.1	745.9	
toluene	744.6	745.5	749.9	750.2	
1, <i>trans</i> -2, <i>cis</i> -3-trimethylcyclopentane	747.6	747.8	752.7	751.1	
2,5-dimethyl-2-hexene	750.4	749.9			
2,3,4-trimethylpentane	752.0	752.4	754.5	755.1	
unidentified	753.1				
unidentified	754.2				
2,3,3-trimethylpentane	757.8	759.4			
2,3-dimethylhexane	760.0	760.1	761.6	761.5	
2-methyl-3-ethylpentane	761.3	761.4	763.4	763.5	
1,1,2-trimethylcyclopentane	763.0	763.2			
2-methylheptane	764.8	764.9	765.1	765.2	
4-methylheptane	767.2	767.2	767.7	767.7	
ethylidenecyclopentane	769.2	768.9 <sup>c</sup>	769.6	771.4 <sup>c</sup>	
3,4-dimethylhexane	770.6	770.6	772.9	772.6	
3-methylheptane	772.3	772.3 <sup>e</sup>	775.6	773.6 <sup>e</sup>	
3-methyl-3-ethylpentane	774.6	774.0	777.4	777.5	
2,2,5-trimethylhexane	775.7	776.3			
unidentified	777.7				
2-methyl-3-ethyl-2-pentene	778.5	778.4	779.2	780.0	
unidentified	780.1				
1-octene	781.2	781.2			
<i>trans</i> -4-octene	782.7	783.6	783.1	783.9	
1, <i>cis</i> -3-dimethylcyclohexane	784.7	785.0	787.2	789.9	
1,1-dimethylcyclohexane	786.5	787.0	789.0	792.0	
2,3-dimethyl-2-hexene	787.6	788.8	791.4	790.2	
2,2,4-trimethylhexane	788.9	789.1	792.6	791.7	
1-methyl, <i>cis</i> -3-ethylcyclopentane	790.1	790.3	794.6	794.1	
1-methyl, <i>trans</i> -3-ethylcyclopentane	790.7	790.3 <sup>c</sup>			
1-methyl, <i>trans</i> -2-ethylcyclopentane	792.6	790.9 <sup>b</sup>			
unidentified	793.6				
1-methyl-1-ethylcyclopentane	795.4	794.7 <sup>b</sup>			
<i>trans</i> -2-octene	797.2	797.7	797.0	797.9	
octane					
1, <i>trans</i> -2-dimethylcyclohexane	801.6	801.8	805.3	807.5	
1, <i>cis</i> -2, <i>cis</i> -3-trimethylcyclopentane	803.1	802.2	807.3	807.7	
1, <i>cis</i> -4-dimethylcyclohexane	805.2	805.2	810.5	810.5	
1, <i>trans</i> -3-dimethylcyclohexane	806.8	805.6			
2,4,4-trimethylhexane	808.7	807.7			
unidentified	810.2				
2,3,5-trimethylhexane	812.0	812.0	813.7	813.7	
isopropylcyclopentane	814.2	812.2	817.0	817.1	
2,2-dimethylheptane	815.9	815.4	818.4	816.5	
4-vinylcyclohexene	818.5	817.8 <sup>c</sup>			
2,4-dimethylheptane	820.5	820.2 <sup>c</sup>	820.1	820.8 <sup>c</sup>	
1-methyl, <i>cis</i> -2-ethylcyclopentane	822.6	821.3 <sup>c</sup>	824.8	826.2 <sup>c</sup>	
2,2-dimethyl-3-ethylpentane	825.2	822.2 <sup>e</sup>	827.3	826.4 <sup>e</sup>	
2,6-dimethylheptane	826.8	827.2 <sup>e</sup>	829.5	827.7 <sup>e</sup>	
2,4-dimethyl-1-heptene	828.7	828.9 <sup>c</sup>	830.3	830.5 <sup>c</sup>	
propylcyclopentane			834.0	834.5	
1, <i>cis</i> -2-dimethylcyclohexane	829.9	830.0	835.2	835.4	
ethylcyclohexane	832.2	834.4	839.9	839.7	

Table III (Continued)

	$I_{50}$		$I_{70}$		confirmation by MS
	measd	RC <sup>f</sup>	measd	RC <sup>f</sup>	
ethylbenzene	833.8	833.6 <sup>d</sup>	839.6	838.9 <sup>d</sup>	+
2,3,3-trimethylhexane	840.0	840.0 <sup>e</sup>	843.9	843.7 <sup>e</sup>	
1,1,3-trimethylcyclohexane	841.6	840.4	848.1	846.0	
2-methyl-3-ethylhexane	844.2	843.7 <sup>e</sup>	845.8	845.8 <sup>e</sup>	
2,3,4-trimethylhexane	847.6	846.6 <sup>e</sup>	848.8	849.8 <sup>e</sup>	
<i>p</i> -xylene	848.3	848.2 <sup>d</sup>	853.8	853.3 <sup>d</sup>	+
<i>m</i> -xylene	850.4	850.4 <sup>d</sup>	855.9	855.3 <sup>d</sup>	+
2,2,3,3-tetramethylpentane	852.9	852.1			
3-methyl-4-ethylhexane	854.3	854.8 <sup>e</sup>			
2,3-dimethylheptane	856.4	854.8 <sup>e</sup>			
4-ethylheptane	857.8	857.5 <sup>e</sup>			
2,3,3,4-tetramethylpentane	859.8	858.9 <sup>e</sup>			
styrene	862.6	862.9 <sup>c</sup>	870.8	869.8 <sup>c</sup>	+
2-methyloctane	864.4	864.7 <sup>e</sup>	865.0	865.0 <sup>e</sup>	
3-ethylheptane	866.9	866.9 <sup>e</sup>	866.4	867.8 <sup>e</sup>	
<i>o</i> -xylene	868.7	868.7 <sup>d</sup>	875.0	874.4 <sup>d</sup>	+
3-methyloctane	870.1	870.3 <sup>e</sup>	870.8	871.0 <sup>e</sup>	
unidentified	882.0				
1,1,2-trimethylcyclohexane	883.4	883.7 <sup>b</sup>			
unidentified	884.6				
nonene	889.5		895.7		+
isopropylbenzene	893.2	893.1 <sup>d</sup>	898.9	898.4 <sup>d</sup>	+
nonane					
unidentified	903.7		912.3		
propylbenzene	921.4	921.3 <sup>d</sup>	927.6	926.9 <sup>d</sup>	+
1-methyl-3-ethylbenzene	935.6	935.8 <sup>d</sup>	941.0	940.6 <sup>d</sup>	+
1-methyl-4-ethylbenzene	937.2	937.2 <sup>d</sup>	943.2	942.6 <sup>d</sup>	+
$\alpha$ -methylstyrene	947.8		953.5		+
1-methyl-2-ethylbenzene	949.7	949.8 <sup>d</sup>	956.1	955.4 <sup>d</sup>	+
$\beta$ -methylstyrene	952.9				+
1,3,5-trimethylbenzene			958.9	959.6 <sup>d</sup>	+
indan	963.2				+
<i>m</i> -methylstyrene	964.9		969.9		+
<i>p</i> -methylstyrene	966.3		973.2		+
1,2,4-trimethylbenzene	970.7	971.1 <sup>d</sup>	974.6	976.8 <sup>d</sup>	+
dicyclopentadiene	982.0				+
<i>o</i> -methylstyrene	990.2		992.2		+
indene	994.2		997.2		+
1-methyl-4-isopropylbenzene	997.7	996.4 <sup>d</sup>	1003.2	1001.7 <sup>d</sup>	
decane					
1-methyl-2-isopropylbenzene	1005.3	1002.5 <sup>d</sup>	1004.4	1007.8 <sup>d</sup>	
1,3-dimethyl-5-ethylbenzene	1038.9	1036.9 <sup>d</sup>			
unidentified	1040.0				
unidentified	1040.8				
1-methyl-3- <i>tert</i> -butylbenzene	1046.5	1044.0 <sup>d</sup>	1047.3	1048.8 <sup>d</sup>	
1,4-dimethyl-2-ethylbenzene	1047.6	1046.5 <sup>d</sup>	1050.5	1051.6 <sup>d</sup>	
1,2-dimethyl-4-ethylbenzene	1057.7	1056.4 <sup>d</sup>	1067.2	1062.1 <sup>d</sup>	
undecane					

<sup>a</sup> Length 100 m, i.d. 0.25 mm, inlet pressure 0.25 MPa, split ratio 1:350. Number of measurements: 4. Mean standard deviation less than 0.5 index units. <sup>b</sup> Data from Loewenguth and Tourres (1968). <sup>c</sup> Data from Hively and Hinton (1968). <sup>d</sup> Data from Soják and Rijk (1976). <sup>e</sup> Data from Tourres (1967). <sup>f</sup> Tabulated by Rijk and Cramers (1974).

of metal sulfides. The sulfidic film inhibits the secondary reactions which lead to the formation of coke.

The main function of the steam is to reduce the partial pressure of the reactants and in this way to reduce the formation of high-boiling products and coke. The latter products are formed by condensation and polymerization reactions, which take place in the highly reactive system of aromatic and olefinic hydrocarbons. The presence of carbon oxides, particularly carbon monoxide, proves that steam is not only an inert diluent but also a reactant in a reactor with a large ratio of inner surface to volume.

The composition of the product mixtures from stainless steel and quartz reactors is different. In the former one there is a lower yield of methane and ethane, while liquid products boiling approximately above 200 °C are practically absent. The lower content of light alkanes might be explained by a shift reaction between alkanes, or better, their radicals, such as methylene or methyl radicals, and steam at the inner surface of the reactor (Bajus et al.,

1979a,b). The formation of ethene from ethyl or methylene radicals cannot be excluded.

All identified aromatic hydrocarbons are produced in the pyrolysis. Benzene, toluene, and aromatic hydrocarbons C<sub>8</sub> initially present in the feed, and also produced by pyrolysis, pass partly unchanged through the process. Among the reaction products from the stainless steel reactor, from the higher aromatics (C<sub>8</sub>–C<sub>11</sub>) only alkylated benzenes, indanes, and indenenes were found (Table IV). Dicyclopentadiene is also present. Styrene and indene with their homologues predominate. No condensed aromatics with higher molecular mass were observed, such as naphthalene, biphenyls, and their homologues, which are known to be precursors to coke. The absence of these hydrocarbons is definitely in correlation with the nature of the increased inner surface of the stainless steel reactor and with the secondary reactions, which lead to carbon monoxide and hydrogen. This absence may be explained by the following suppositions. Condensed aromatics, if

Table IV. Composition of the Aromatic C<sub>8</sub>-C<sub>11</sub> Hydrocarbon Fraction (% Mass)

styrene	38.79
isopropylbenzene	1.86
propylbenzene	3.09
1-methyl-3-ethylbenzene	3.92
1-methyl-4-ethylbenzene	2.14
$\alpha$ -methylstyrene	1.72
1-methyl-2-ethylbenzene	1.40
$\beta$ -methylstyrene	1.29
1,3,5-trimethylbenzene	0.29
indan	2.36
<i>m</i> -methylstyrene	5.19
<i>p</i> -methylstyrene	2.58
1,2,4-trimethylbenzene	1.26
dicyclopentadiene	5.26
<i>o</i> -methylstyrene	2.29
indene	11.80
1-methyl-4-isopropylbenzene	0.43
1-methyl-2-isopropylbenzene	1.14
1,3-dimethyl-5-ethylbenzene	5.26
1-methyl-3- <i>tert</i> -butylbenzene	1.72
1,4-dimethyl-3-ethylbenzene	0.86
1,2-dimethyl-4-ethylbenzene	5.45

formed, are preferentially adsorbed on the inner surface of the metal reactor. Here they react directly with steam or they are further degraded to coke, and it is this coke which reacts with the steam. Both assumptions are acceptable, and both processes can take place at the same time.

### Conclusions

In the stainless steel reactor less methane and ethane are produced than in a quartz reactor working under the same conditions. The yields of ethene are essentially the same. An increase of the ratio of steam to hydrocarbon increases the yield of ethene.

Among the liquid products from the stainless steel reactor, condensed aromatics of naphthalene and biphenyl types are absent. On the other hand, high amounts of carbon monoxide are formed. The absence of condensed aromatic hydrocarbons with higher molecular mass is connected with the metal surface, which promotes sec-

ondary reactions leading to carbon monoxide and hydrogen. A possible explanation is based on the assumption that higher aromatic hydrocarbons are adsorbed on the surface. Here they are either directly converted with steam to carbon monoxide and hydrogen, or they are further dehydrogenated to coke. The coke is then converted to carbon monoxide and hydrogen. Both processes may take place simultaneously.

In steam cracking, straight-run naphtha produces less coke than individual hydrocarbons. The cause of this behavior is the presence of sulfur compounds in straight-run naphthas. The decomposition products of sulfur compounds in the straight-run naphtha form a protective film of metal sulfides on the metal surface. This film inhibits the formation of coke.

### Literature Cited

- Bajus, M.; Veselý, V. *Ropa Uhlí* **1976**, *18*, 126.  
 Bajus, M.; Veselý, V. *Netekhimiya* **1979**, *19*, 523.  
 Bajus, M.; Veselý, V.; Laclercq, P. A.; Rijks, J. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1979a**, *18*, 30.  
 Bajus, M.; Veselý, V.; Laclercq, P. A.; Rijks, J. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1979b**, *18*, 135.  
 Brown, S. M.; Albright, L. F. *ACS Symp. Ser.* **1976**, No. 32, 296.  
 Crynes, B. L.; Albright, L. F. *Ind. Eng. Chem. Process Des. Dev.* **1969**, *8*, 25.  
 Dunkleman, J. J.; Albright, L. F. *ACS Symp. Ser.* **1976a**, No. 32, 241.  
 Dunkleman, J. J.; Albright, L. F. *ACS Symp. Ser.* **1976b**, No. 32, 261.  
 Ghaly, M. A.; Crynes, B. L. *ACS Symp. Ser.* **1976**, No. 32, 218.  
 Hively, R. A.; Hinton, R. E. *J. Gas Chromatogr.* **1968**, *6*, 203.  
 Hougen, O. A.; Watson, K. M. "Chemical Process Principles"; Wiley: New York, 1947; Vol. III, p 884.  
 Hurd, Ch. D.; Eilers, L. K. *Ind. Eng. Chem.* **1934**, *26*, 776.  
 Hurd, Ch. D.; Pilgrim, F. D. *J. Am. Chem. Soc.* **1933**, *55*, 4902.  
 Leferink, J. G.; Leclercq, P. A. *J. Chromatogr.* **1974**, *91*, 385.  
 Loewenguth, J. C.; Tourres, D. A. *Z. Anal. Chem.* **1968**, *236*, 170.  
 Melikadze, M. M.; Safichanov, M. S.; Schkolnik, B. L. *Azerb. Neft. Khoz.* **1975**, *12*, 48.  
 Rijks, J. A.; Cramers, C. A. *Chromatographia* **1974**, *7*, 99.  
 Soják, L.; Rijks, J. A. *J. Chromatogr.* **1976**, *119*, 505.  
 Tamai, Y.; Nishiyama, Y. *Bull. Jpn. Pet. Inst.* **1970**, *12*, 6.  
 Tourres, D. A. *J. Chromatogr.* **1967**, *30*, 357.

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