

Steam Cracking of Hydrocarbons. 4. Analysis of High-Boiling Products from Naphtha in a Quartz Reactor

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Part 3 of this series reported on the steam cracking of straight-run naphtha in a stainless steel and a quartz reactor. High-boiling polynuclear aromatic hydrocarbons were formed in a quartz reactor but were not found as products from a stainless-steel reactor. In this paper the analysis of the polynuclear aromatic hydrocarbons is discussed. The high-boiling fraction was separated by high performance liquid chromatography and by capillary gas chromatography. About 200 of the compounds present were separated by the latter method. Twenty profiling compounds, with boiling points up to 462 °C, were identified by the coelution technique and by combined gas chromatography/mass spectrometry. The influence of the wall effects on the proceeding of secondary reactions in metal and quartz reactors is discussed.

Introduction

Although the conversion of hydrocarbons by pyrolysis or steam cracking in a number of publications is supposed to be a purely homogeneous reaction proceeding in the gaseous phase, in other studies the influence of the reactor wall was not neglected. The wall effect depends in a decisive way on the chemical composition of the reactor material, the ratio of surface to volume of the reactor, and the chemical activation or passivation of the surface by different compounds.

In metal reactors, especially in stainless steel reactors, the reactions at the wall are much more important than in glass reactors. Hurd and Eilers (1934), Dunklema and Albright (1976a,b), Brown and Albright (1976), and Bajus et al. (1980) have unequivocally shown that the wall effect significantly influences the formation of coke, high molecular compounds, carbon oxides, and hydrogen. The activation energies in the range of 62.8–201.3 kJ mol⁻¹, for the conversion of ethane, propane, ethene, and propene in an Incoloy reactor (Brown and Albright, 1976) and of heptane and methylcyclohexane in a stainless steel reactor (Bajus et al., 1979a,b) are lower than those found for gaseous hydrocarbons (213.5–276.3 kJ mol⁻¹) in a Vycor glass reactor (Brown and Albright, 1976). Compared to a quartz reactor, steam cracking of straight-run naphtha (Bajus et al., 1980) in a stainless steel reactor yields less methane and ethane while no higher polyaromatics are observed. In quartz reactors, however, an appreciable fraction of aromatics, boiling above 200 °C, is formed. A further study of the wall effect on the formation of polynuclear aromatic hydrocarbons necessitates knowing the composition of the liquid product mixtures from metal as well as quartz reactors.

Pyrolytic oils are commonly fractionated by vacuum distillation, yielding liquid products and solid residues

(pyrolytic resins). The lower-boiling fractions have been analyzed by capillary gas chromatography in combination with mass spectrometry and infrared spectroscopy (Artyukhovskaya et al., 1976). Pyrolytic resins are either decomposed thermally or transformed catalytically in the presence of hydrogen (Popl and Kuraš, 1977). They are analyzed by gas chromatography and mass spectrometry. Attention has been devoted especially to the separation of alkynaphthalenes by gas chromatography (Vindergauz and Vigalok, 1971; Walker and Ahlberg, 1963; Mostecký et al., 1970; Soják and Barnoky, 1974) because they are relatively abundant in the pyrolytic oils. The identification of some higher polyaromatic hydrocarbons by means of gas (Fike, 1973) and liquid chromatography (Fox and Staley, 1976; Broden, 1976; Popl et al., 1977) has been reported.

The aim of this study is to separate and identify the compounds present in the high-boiling product mixture by liquid chromatography and high-resolution capillary gas chromatography. The influence of the wall on the course of secondary reactions in metal and quartz reactors is discussed, notably on the gasification of polynuclear aromatics to carbon monoxide and hydrogen.

Materials and Methods

The experimental equipment used for the steam cracking of the straight-run naphtha was the same as reported previously (Bajus et al., 1979a). The tubular flow reactors were made from stainless steel and quartz. The ratio of inner surface to volume of the reactors was 6.65 cm⁻¹ for stainless steel and 4.82 cm⁻¹ for quartz. The straight-run naphtha originated from Romashkino crude oil. The distillation range was 34–125 °C and the sulfur content 0.016% (mass). Steam was used as diluent. The operating conditions for the steam cracking are given in a previous paper (Bajus et al., 1980).

For the analysis a model sample of high-boiling oil, a distillation fraction of the liquid product mixture of straight-run naphtha from a quartz reactor, was used. After dilution with benzene and homogenation by ultrasonification this sample was analyzed by high performance liquid chromatography and capillary gas chromatography. Standard hydrocarbons (American Petroleum Institute, Pittsburgh, Pa., and Fluka, Buchs, Switzerland) were used for the identification.

Liquid Chromatography. The separation of the high-boiling oil constituents was performed on a liquid chromatograph, constructed from custom-made and commercially available parts. It consisted of a reciprocating high-pressure pump (Type DMP 1515, Orlita, Giessen, West Germany), an injection valve (Valco, Houston, Texas) equipped with a sample loop of 41 μL , and a variable wavelength UV detector (Type PM2 DLC, Zeiss, Oberkochen, West Germany) operated at 254 nm. The column, 300 mm \times 4.6 mm i.d., was filled by means of a balanced density slurry technique with LiChrosorb SI-60 (Merck, Darmstadt, West Germany) with a mean particle size of 5 μm . The mobile phase, 2,2,4-trimethylpentane (p.a. quality, Merck, Darmstadt, West Germany) was dried with molecular sieve 3 Å and degassed by ultrasonification immediately before use. A volumetric flow rate of 1 $\text{cm}^3 \text{min}^{-1}$ was applied. The high-boiling oil was dissolved in the mobile phase. Separations were carried out at room temperature.

Gas Chromatography. The experiments were performed on a Hewlett-Packard (Palo Alto, Calif.) Model 5750 gas chromatograph. A glass capillary column, 21 m \times 0.22 mm i.d., prepared according to Cramers and Vermeer (1977) and coated with OV 225 as stationary phase, was used. The separations were carried out under the following conditions: carrier gas, nitrogen; inlet pressure, 200 kPa; flame ionization detector at 260 $^{\circ}\text{C}$; sample size, 4 μL ; injector at 240 $^{\circ}\text{C}$ with a split ratio of 1:300. The column was operated at an initial temperature of 50 $^{\circ}\text{C}$ during 20 min, then heated at a rate of 2 $^{\circ}\text{C}/\text{min}$ up to a constant temperature of 225 $^{\circ}\text{C}$.

The same column was used at the same operating conditions in an on-line gas chromatograph/mass spectrometer combination (Leferink and Leclercq, 1974), but helium was used instead of nitrogen.

Results and Discussion

Because of the high-boiling range of the oil, high-performance liquid chromatography was initially the method of choice for the separation of the mixture.

Liquid Chromatography. Capacity factors and hence the resolution of components eluting from silica gel columns in liquid-solid chromatography, using apolar mobile phases such as 2,2,4-trimethylpentane, are markedly influenced by the water content of the mobile phase and the adsorbent.

Separations were performed with 2,2,4-trimethylpentane (isooctane) partly saturated with water (25%) as the mobile phase. For this purpose wet 2,2,4-trimethylpentane was mixed with dry 2,2,4-trimethylpentane (dried over molecular sieve 3 Å). In order to obtain constant capacity factors the column was rinsed with acetone from time to time (5–10 injections of 50 μL of acetone). In this way strongly absorbed components from sample injections could be eluted from the column too.

A chromatogram of the separation of the high-boiling oil constituents by liquid chromatography is shown in Figure 1. The relative retention times for the individual chromatographic peaks obtained in a stable phase system are given in Table I. The chromatogram contains 23

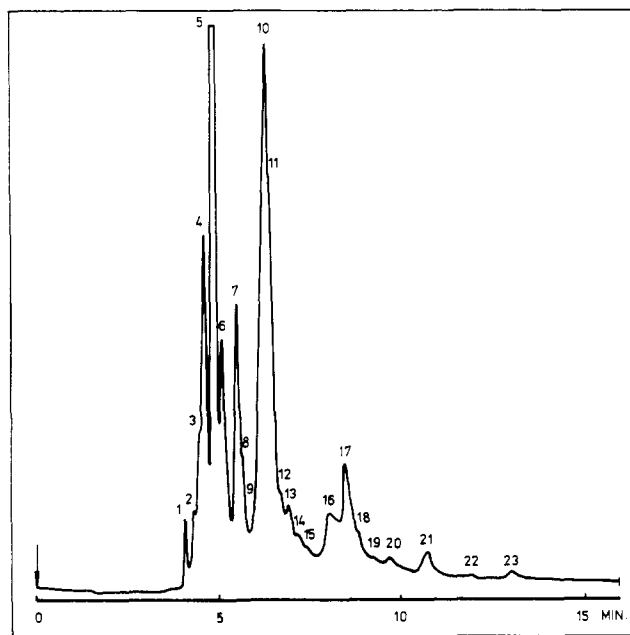


Figure 1. Liquid chromatogram of the high-boiling oil on LiChrosorb SI-60; mobile phase: isooctane. (Cf. Table I for the identity of the peaks.)

Table I. Relative Retention Times, $r_{x,\text{biphenyl}}$, of the Separated High-Boiling Oil Components and Standard Compounds Measured by Liquid Chromatography^a

peak no. (Figure 1)	compound	$r_{x,\text{biphenyl}}$	
		high-boiling oil	standard
1	benzene	0.73	0.72
2	indan; 1,1-dimethylindan, tetralin	0.77	0.75
5	naphthalene; 1- and 2-methylnaphthalene	0.87	0.87
7	biphenyl	1.00	1.00
10	fluorene, phenanthrene, anthracene	1.14	1.14
11	pyrene; triphenylmethane	1.17	1.17
18	chrysene	1.61	1.51
	1,3,5-triphenylbenzene	-	2.00

^a Number of measurements was 6 and 10 for the oil and standards, respectively. The following peaks were not identified (peak no., $r_{x,\text{biphenyl}}$): 3, 0.81; 4, 0.83; 6, 0.92; 8, 1.03; 9, 1.08; 12, 1.22; 13, 1.27; 14, 1.31; 15, 1.34; 16, 1.46; 17, 1.56; 19, 1.69; 20, 1.77; 21, 1.96; 22, 2.10.

peaks. For the identification, the relative retention times of standard hydrocarbons (cf. Table I) were compared to those of the peaks from the sample. Table I shows that on LiChrosorb SI-60 no separation could be accomplished for indan and its homologues, naphthalene and its homologues, fluorene-phenanthrene-anthracene and pyrene-triphenylmethane. Only six peaks could be identified.

Liquid chromatography can be applied as a preseparation method for group separation of classes of compounds (Suatoni and Garber, 1976). From our experiments, however, it must be concluded that the analysis of polynuclear aromatic hydrocarbons by means of high performance liquid chromatography is not very promising. Therefore we decided to investigate the possibilities of capillary gas chromatography for this purpose.

Gas Chromatography. The sample of high-boiling oil was analyzed on a glass capillary OV 225 column. A representative chromatogram is shown in Figures 2–5. Within an analysis time of 2 h about 200 compounds were partly

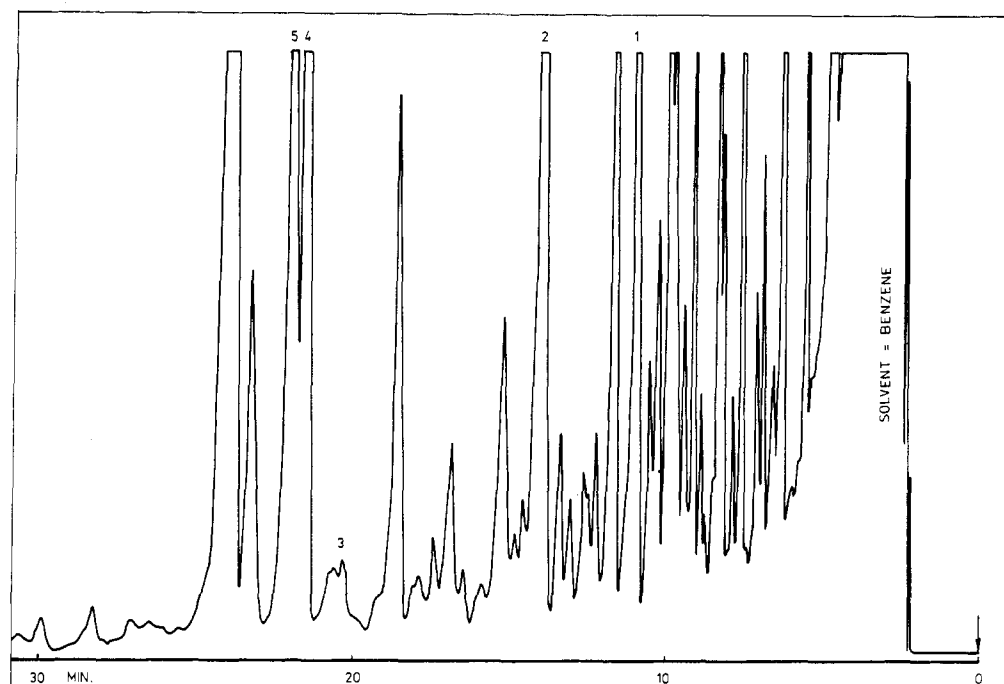


Figure 2. First part of the gas chromatogram of the high-boiling oil on a capillary OV 225 column. (Cf. Table II for the identity of the peaks.)

Table II. Identification of Some Compounds in the High-Boiling Oil on the Capillary OV 225 Column

hydrocarbon	identification by	
	standard	MS
1. indan	+	+
2. indene	+	+
3. tetralin	+	+
4. 1-methylindene		+
5. 2- or 3-methylindene		+
6. naphthalene	+	+
7. cyclohexylbenzene	+	
8. 2-methylnaphthalene	+	+
9. 1-methylnaphthalene	+	+
10. biphenyl	+	+
11. 2-ethylnaphthalene		+
12. 3-methylbiphenyl		+
13. diphenylmethane		+
14. fluorene	+	+
15. 2-ethylbiphenyl		+
16. phenanthrene	+	+
17. anthracene	+	
18. triphenylmethane	+	
19. pyrene	+	+
20. triphenylbenzene	+	

or completely separated. The identification was done by comparing the chromatograms (peak profiles) of the original sample with those of the sample after addition of the individual standards (coelution method). Combined gas chromatography/mass spectrometry with the same column was used either for confirmation of the identity of compounds already characterized by gas chromatography or for identification of unknowns. In this way 20 hydrocarbons could be identified as shown in Table II. The lack of standards or accurate literature data and mass spectra as well as the wide range of boiling points of the compounds in the sample (e.g., triphenylbenzene, boiling point 462 °C) are the most serious limitations for the qualitative analysis of the high-boiling oil. An additional problem is the presence of a number of isomers in rather low concentrations.

By a careful selection of the operating conditions for the OV 225 column the lower boiling aromatic compounds, with a carbon number between 6 and 11, could also be

Table III. Composition of the Liquid Product Mixture (% Mass) from the Steam Cracking of Naphtha (Yields Relative to the Feed)^a

hydrocarbon	reactor material			
	quartz		stainless steel	
	residence time, s		residence time, s	
	0.18	0.29	0.18	0.32
benzene	1.15	0.93	2.16	1.89
toluene	0.67	0.94	1.77	0.85
ethylbenzene; <i>p</i> - and <i>m</i> -xylene	0.21	0.14	1.23	0.15
<i>o</i> -xylene	0.08	0.08		
styrene	0.24	0.35	0.72	0.32
indan	0.29	0.25	0.05	0.02
indene	0.31	0.50	0.21	0.10
naphthalene	0.76	1.06		
2-methylnaphthalene	0.32	0.33		
1-methylnaphthalene	0.29	0.32		
biphenyl	0.14	0.13		
2-ethylnaphthalene	0.09	0.10		
3-methylbiphenyl	0.16	0.27		
fluorene	0.13	0.18		
phenanthrene	0.53	0.29		

^a Temperature: 780 °C. Mass ratio of water to feed 0.5:1.

separated. This was done to enable the quantitation of these compounds for studying the mechanism of the steam cracking of straight-run naphtha. In this way were determined the yields of the most abundant aromatic hydrocarbons in the product mixture from the steam cracking of straight-run naphtha in a quartz reactor.

The variation of the amounts of indene, naphthalene and its homologues, and phenanthrene, which are present together with benzene, toluene, and styrene, with the residence time is given in Table III.

Reaction Mechanisms. The results of the qualitative and quantitative analysis show unequivocally that in the steam cracking of straight-run naphtha in a quartz reactor, aromatic hydrocarbons are formed: for instance, naphthalene, biphenyl, fluorene, phenanthrene, anthracene, pyrene, chrysene, di- and triphenylmethane, triphenyl-

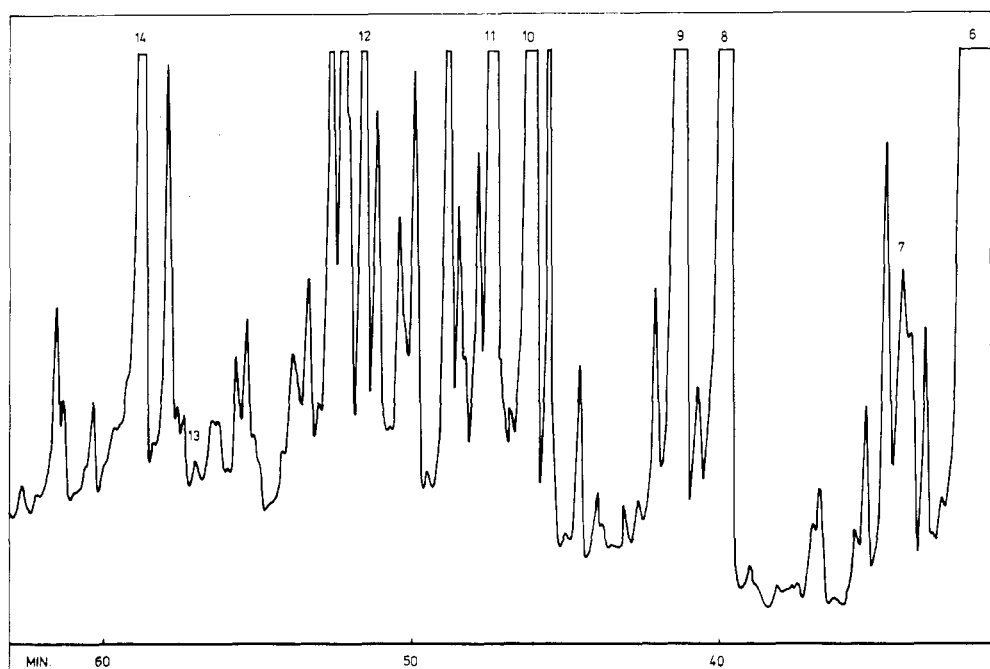


Figure 3. Second part of the gas chromatogram of the high-boiling oil on a capillary OV 225 column. (Cf. Table II for the identity of the peaks.)

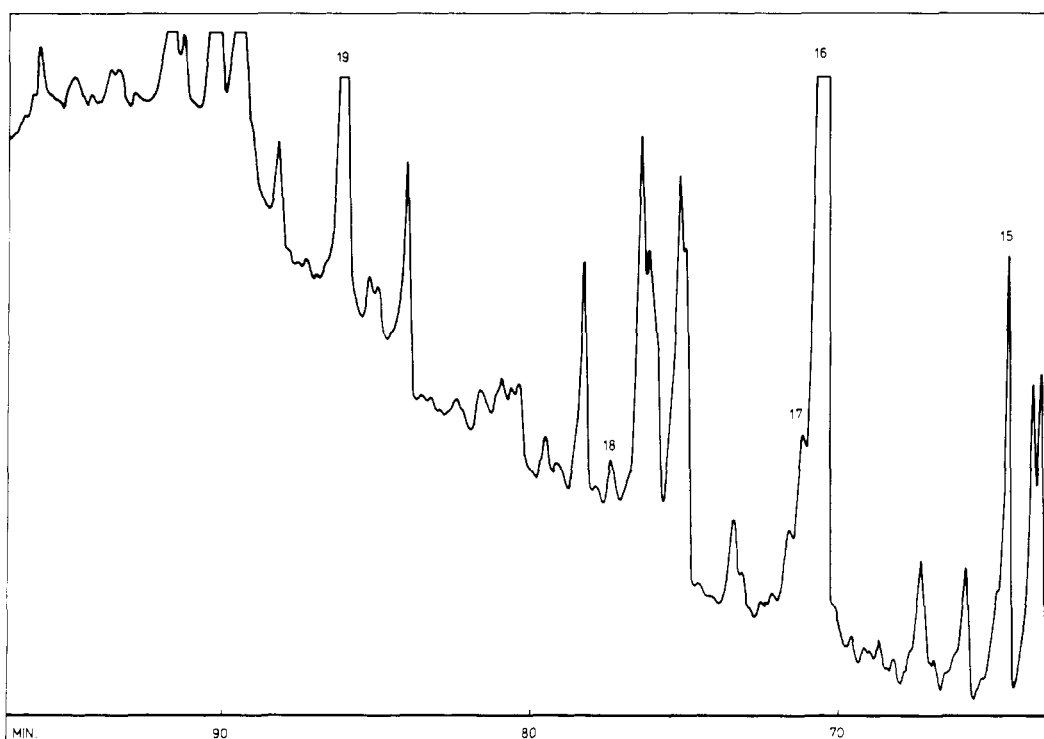


Figure 4. Third part of the gas chromatogram of the high-boiling oil on a capillary OV 225 column. (Cf. Table II for the identity of the peaks.)

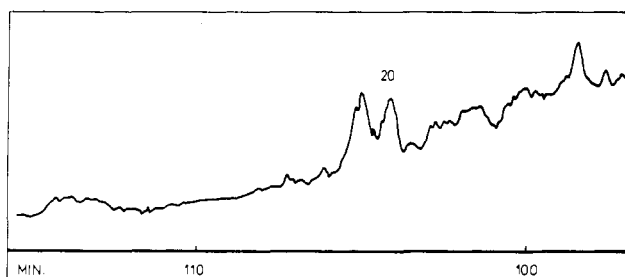
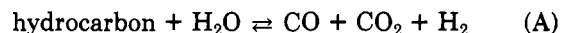


Figure 5. Fourth part of the gas chromatogram of the high-boiling oil on a capillary OV 225 column. (Cf. Table II for the identity of the peaks.)

benzene, and their homologues. In the liquid product mixture from the steam cracking of the same naphtha at identical conditions in a stainless steel reactor (Bajus et al., 1980) only styrene and its homologues, ethyltoluenes, indan, and indenenes, but no higher aromatic hydrocarbons were found (Table III). As the conversion of the straight-run naphtha proceeds in both reactors in the presence of steam, aromatic hydrocarbons may react with steam to carbon oxides and hydrogen according to eq A



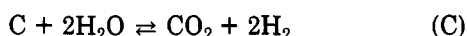
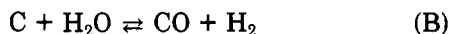
or they may be converted by consecutive degradations to carbon, which is deposited as coke on the inner surface of

Table IV. Yields of Carbon Monoxide and Hydrogen (% Mass) from the Steam Cracking of Naphtha^a

	reactor material							
	quartz				stainless steel			
	residence time, s				residence time, s			
	0.184	0.22	0.29	0.36	0.165	0.170	0.175	
carbon	0.08	0.17	0.15	0.22	3.75	4.48	3.33	
monoxide								
hydrogen	0.71	0.83	0.74	0.51	1.07	0.77	0.84	

^a Temperature: 780 °C. Mass ratio of water to feed 0.5:1.

the reactor. This coke may react with steam according to (B) and (C)



Earlier results (Bajus et al., 1979a,b, 1980) show that the reactions of hydrocarbons with steam are in a decisive way dependent on the quality of the inner surface of the reactor. The formation of polyaromatic hydrocarbons on one side and the low yields of carbon monoxide on the other side (Table IV) prove that the influence of the surface of a quartz reactor on the gasification reactions is negligible. The surface of a stainless steel reactor, however, significantly promotes the transformation of aromatics and carbon to carbon monoxide and hydrogen (Table IV). The catalytic effect of the wall in a stainless steel tubular reactor is also greater in surface reactions, as evidenced by the partial oxidation of light alkanes (Mahajan et al., 1977) below 560 °C, in comparison with a glass reactor.

Condensed aromatics are known to be more prone to coking than alkanes, cycloalkanes, and olefins. The quality and size of the inner surface of the reaction system play a decisive role. The metal surface may be passivated by active chemical compounds, e.g., sulfur compounds, which are present in straight-run naphthas. Because of the inhibition effect of sulfur compounds the conversion of aromatic hydrocarbons may be directed to gasification according to reaction A instead of formation of coke and gasification according to reactions B and C.

Conclusion

In the steam cracking of straight-run naphtha in a tubular quartz flow reactor, products with distillation end point up to 450 °C are formed, such as naphthalene, biphenyl, fluorene, phenanthrene, anthracene, pyrene, chrysene, diphenylmethane, triphenylmethane, triphenylbenzene, and their homologues. These heavy compounds are not present among the products from a stainless steel reactor. This confirms our former supposition (Bajus et al., 1980) that the catalytic effect of the wall in a stainless steel reactor, leading to the conversion of aromatics and carbon to carbon monoxide and hydrogen, is much more important than the contribution of the wall in a quartz reactor. As shown in this paper, the source of carbon oxides may be condensed polyaromatic hydrocarbons, whose gasification with steam is thermodynamically possible.

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