atmospheres) shows that the specific yield may be increased by reducing the hourly gas throughput 50 percent. This, however, also reduces the space-time yield.

In preparations similar to the thoria-alumina catalysts, aluminum oxide-zinc oxide catalysts also were made by precipitating the two components separately and mixing the washed precipitates. An aluminum oxide-zinc oxide catalyst (mole ratio 1:1) prepared by separate precipitation with sodium carbonate had a bulk density of 0.32 (as against 0.84). Catalysts of this type produce a low space-time yield. When a test was made in which a layer of zinc oxide preceded a layer of aluminum oxide, methane was the principal hydrocarbon.

ON THORIA-ALUMINA

Thorium and zinc oxide were precipitated from the nitrates, and aluminum oxide was prepared from the aluminate. The three components were combined in varying proportions. The catalysts thus obtained were tested at 300 atmospheres and 450° C. A typical catalyst containing thorium, aluminum, and zinc oxides in a 2:0.4:1 ratio (59:11:30 parts by weight) produced the results tabulated in row 17, table 11. The yields included 59.2 grams C_5+ and 31.7 grams i-C_4 hydrocarbons per cubic meter inert-free feed gas. These results are similar to those obtained with the thorium oxide-zinc oxide catalysts (alumina-free) summarized in rows 10 and 11. The C_5+ hydrocarbon yield is larger and the iso-C_4 hydrocarbon yield smaller in experiment 17 than in tests of thoria-alumina (zinc-free) catalysts (see table 8).

EFFECT OF CHROMIUM OXIDE

ON THORIA

The two components in this catalyst were coprecipitated by sodium carbonate from a solution of the metal nitrates. The precipitate was dried at 300° C. and was operated at 450° C. and 300 atmospheres of synthesis gas containing 51.6 percent carbon monoxide and 39.1 percent hydrogen. The iso-C_4 hydrocarbon yield (table 12, row 1) was higher than that obtained from a thoria one-component catalyst (table 8, row 1), but was considerably smaller than that produced by the $100ThO_2$–$20Al_2O_3$ catalyst (table 8, row 5).

ON ALUMINA

The activity of an aluminum oxide-chromium oxide catalyst was tested at 30 atmospheres and temperatures up to 500° C. The relatively low activity of these catalysts and their limited tendency to form carbon made operation at 500° C. possible. The specific yields of liquid hydrocarbons were small (5 to 10 grams per cubic meter of synthesis gas). Nevertheless, this type of catalyst is of interest because the liquid hydrocarbons obtained are almost entirely aromatic, as described in a later section of this paper.

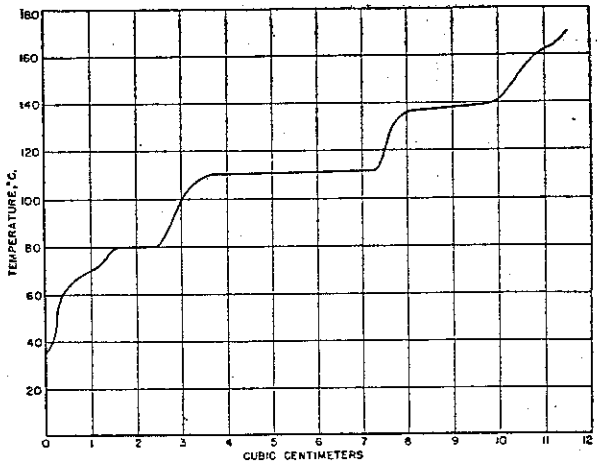

FIGURE 7.—DISTILLATION CURVE OF THE PRODUCT FROM EXPERIMENT 35 (Al_2O_3+ 10% Cr CATALYST, 30 ATMOSPHERES, 500° C.).

The refractive index, n_D^{20}, for the total reaction product obtained with the aluminum oxide-chromium oxide catalyst was 1.48 to 1.50. Figure 7 gives the composition of the liquid reaction products analyzed by fractional distillation. The boiling-point curve shows characteristic breaks for benzene, toluene, and xylene. The presence of mesitylene also is indicated. The following refractive indexes were determined for the individual fractions:

° C.	n_D^{20}
<79	1. 4090
79–83	1. 4795
83–109	1. 4619
109–113	1. 4929
113–137	1. 489
137–147	1. 4960
>147	1. 4994

The catalyst used in these experiments contained 10 percent chromium oxide based on alumina. Similar results were obtained with various other catalysts, for example, aluminum oxide-molybdenum oxide catalyst.

EFFECT OF OTHER PROMOTERS ON ThO_2

PHOSPHORIC ACID

Thorium and phosphoric acid in the form of thorium phosphate showed no catalytic activity in hydrocarbon synthesis. On the other hand, some activity was obtained from a powdered

TABLE 12.—*Effect of other promoters (Cr_2O_3, H_3PO_4, Fe, Cu) in the isosynthesis*

Promoter, percent of ThO_2	Pressure, atmospheres	Temperature, °C.	Synthesis gas			Yields, g./m³ inert-free feed gas								
			$CO:H_2$ in in-gas	Conversion, percent		Hydrocarbon products						Alcohols soluble in—		Total liquids+gasol
				CO	H_2	C_5+	i-C_4	n-C_4	C_3	C_2	C_1	Oil	H_2O	
1. Cr_2O_3	300	450	56.1:39.1	69	64	46.8	34.2	3.0	18.3	11.2	11.9	6.8	2.0	111.1
2. 10 Cr_2O_3[a]	30	<500				5–10								
3. H_3PO_4	150	400	[b] 48.0:41.6	(c)	(c)	17.4	[d] 8.5							
4. 0.25 Fe	300	450				38.5	17.3	2.1	9.2	20.7	68	9.4	7.6	84.1
5. 1.25 Fe	300	450				18.9	22.5	1.5	9.2			7.7	1.9	61.7

[a] This was an Al_2O_3–Cr_2O_3 catalyst and contained no ThO_2.
[b] This synthesis gas contained also 3 percent CO_2, 0.2 percent O_2, 7.2 percent N_2.
[c] Contraction was 19 percent.
[d] This value should be compared with 7.3 grams obtained from the same quantity of a standard ThO_2 catalyst tested under similar conditions.

thorium oxide catalyst that was prepared by precipitation with sodium carbonate and dried at 300° C. and then impregnated with phosphoric acid. One hundred grams of thorium oxide and 27 cc. of 88-percent phosphoric acid were combined, cooled, and made into a paste, which was sintered in the oven at 250° C. As shown in table 12, row 3, a small liquid-hydrocarbon yield was obtained. The methane production was high.

Table 13 shows the composition of the end gas obtained in the above experiment (row 1) and similar data for a catalyst containing the same amount of thorium oxide in the absence of phosphoric acid and tested under similar conditions (standard thorium oxide catalyst, row 2). The phosphoric acid-containing catalyst produced a smaller conversion and a larger fraction of methane.

IRON

It is known that straight-chain hydrocarbons are the principal product obtained from iron catalysts at low temperatures in the hydrocarbon synthesis, whereas methane and carbon are the main products obtained at the temperatures and pressures used in isosynthesis.

Table 12 (rows 4 and 5) shows the results obtained when iron (0.25 percent and 1.25 percent, based on thoria) was incorporated into the thoria catalyst. The catalysts were prepared by coprecipitation of the metal constituents with sodium carbonate and washed and dried according to the standard procedure developed for the standard thorium oxide catalyst. Comparison of the data obtained in the tests in rows 4 and 5 of table 12 with those in row 1, table 8 (iron-free catalyst), shows that liquid hydrocarbon and alcohol yields decrease with increasing iron content. The amounts of C_3 and C_4 hydrocarbons remain unchanged, whereas the formation of C_1 and C_2 hydrocarbons (principally methane) increases. It is evident that even small amounts of iron are undesirable. Steps should therefore be taken to avoid the presence of iron carbonyl in the inlet synthesis gas because it decomposes and produces free iron at the temperature of the isosynthesis.

COPPER

The action of copper was studied for a number of reasons. Not only is copper used for lining the converter tubes, but it is known to promote the activity of iron catalysts in hydrocarbon synthesis and to play an important part in the synthesis of methanol. It was of interest to determine whether copper might favor the hydrogenation of unsaturated primary products, thus exercising a stabilizing influence on the course of the reaction. As previously shown in the early pages of this report, the copper lining of the converter tubes appeared to have no effect upon the reaction.

Results obtained with a $100ThO_2$–$0.25Cu$

TABLE 13.—*Effect of phosphoric acid on the catalytic activity of a thoria catalyst (400 °C., 150 atmospheres)*

Catalyst	Contraction, percent	End gas composition, volume percent[a]							
		CO_2	Olefins	O_2	CO	H_2	Hydrocarbons	C–No.	N_2
ThO_2–H_3PO_4	19	11.6	1.3	0.2	40.4	35.1	2.5	1.3	8.9
ThO_2	27	14.1	1.0	0	38.1	36.3	.7	2.0	9.8

[a] Feed gas composition, volume percent: 3.0 CO_2, 0.2 O_2, 48.0 CO, 41.6 H_2, 7.2 N_2.

TABLE 14.—*Conversion of dimethyl- and diethyl-ether over ThO_2 catalyst in the presence of nitrogen and hydrogen at 450° C.*

Gas composition, percent by volume				Pressure, atmospheres	Flow, l./hr.	Duration of test, hours	Average ether conversion, percent	Carbon products, percent of C in converted ether								
								Hydrocarbon products					CO_2	CO	CH_3OH	Losses [a]
Dimethyl	Diethyl	N_2	H_2					C_3+	i-C_4	C_3	C_2	C_1				
16.7		83.3		1	2	66	80.0	0	0	0	2.2	12.7	0	25.2	17.5	42.3
20.3		79.7		30	10	21	73.0	4.1	(b)	~	13.3	~	1.9	45.8	0	34.9
17.5			82.5	30	10	29.5	86.0	33.0	11.5	5.1			1.8	43.8	0	4.8
16.5			83.5	150	10	25	91.8	17.5	24.4	4.2	2.8	14.2	4.0	27.6	0	5.3
	20.4		79.6	30	10	24	71.3	(c)	0	18.5	14.6		4.7	7.8	0	(c)

[a] Consisting of carbon, tar. [b] 300 cc. [c] Total 54.4 percent.

catalyst operated at 75 atmospheres and temperatures of 450° and 475° C. were essentially the same as those obtained in the absence of copper. Experiments with catalysts containing thorium oxide and copper in a 1:1 ratio (30 atmospheres, 450° and 475° C.) produced low molecular-weight hydrocarbon mixtures, increased formation of water-soluble reaction products, and carbon.

CONVERSION OF DIMETHYLETHER

Dimethylether was one of the secondary products obtained in the tests at pressures above 300 atmospheres. Under certain conditions, dimethylether is the principal product at pressures of about 1,000 atmospheres. At high temperatures or in the presence of particularly active catalysts, the yield of dimethylether decreases and that of hydrocarbons increases.

As it was believed possible that dimethylether might be an intermediate product in the isosynthesis, a series of experiments was undertaken to determine the nature of the compounds obtained by passing dimethylether over standard thoria catalyst. The results are summarized in table 14. Passage of a mixture of dimethylether and nitrogen (1:5) at atmospheric pressure and 450° C. produced no iso-C_4 hydrocarbons (experiment 1). In experiment 2 at 30 atmospheres, 300 cc. of iso-C_4 hydrocarbons was obtained. It was observed that this material was produced in the first few hours of the test. Neither iso-butane (determined by distillation) nor iso-butene (determined by formation of yellow precipitate with mercury nitrate) could be detected in the products that formed subsequently. It was also observed that the carbon number of the hydrocarbons obtained decreased as the operating time increased. At the same time, the activity of the catalyst diminished rapidly. The decrease in conversion with time is shown in column A of table 15 and is compared with the constant conversion obtained when nitrogen was replaced by hydrogen [23] (column B). At 450° C. and 30 atmospheres pressure (table 14, experiment 3) some i-C_4 hydrocarbon product was observed, and a slightly larger fraction was obtained at 150 atmospheres, that is, 11.5 and 24.4 percent of the carbon reacted, respectively. The proportion of iso-hydrocarbons produced remained constant during the entire operating period in these experiments.

Similar results were obtained with other catalysts. In the presence of zirconium oxide, 19.3 percent of dimethylether was converted to iso-C_4 hydrocarbons at 150 atmospheres and 450° C. Under the same conditions, the reaction over cerium oxide produced 6.5 percent conversion of dimethylether. On the other hand, no iso-C_4 hydrocarbon fraction was obtained either with zinc or aluminum oxide.

When ethylether was substituted for dimethylether and in admixture with hydrogen passed over a thoria catalyst (table 14, experiment 5), C_2, C_3, and liquid hydrocarbons were obtained, but neither iso-butane nor iso-butene.

Thus, in the presence of excess hydrogen the catalytic decomposition of dimethylether under pressure results in products already obtained by isosynthesis. This is not the case for ethylether.

TABLE 15.—*Effect of nature of carrier gas upon conversion of dimethylether*

Time, hours	(A)	(B)
	N_2 percent	H_2 percent
2	87	88
21	61	
22		90
27	48	
44	33	
48		79
96		86

[23] In both cases the carrier gas was saturated with dimethylether at various temperatures by passing it through liquid dimethylether under pressure.

ANALYTICAL PART

This section includes a rapid survey of the analytical methods used in evaluating experimental results.

In the course of about 300 high-pressure experiments, each of several weeks' and some of several months' duration, daily analyses were made of the inlet and outlet gases. These analyses served to characterize the activity of the catalyst. From time to time, particularly when a change in experimental conditions was involved or when the outlet gas analysis indicated a change in the activity of the catalyst, the composition of the entire reaction product was determined.

The methane was present in the tail gas and was determined by gas analysis. Calculation of the carbon number indicated whether any higher hydrocarbons were present in the end gas. The material in the active charcoal trap was determined as follows: The charcoal trap was heated as usual in a slow current of hydrogen under diminished pressure (for example, a few millimeters of mercury), and the products were condensed in receivers cooled either in a mixture of carbon dioxide and acetone or in liquid air. The receivers were carefully warmed to room temperature, with refluxing when necessary. The gases liberated in this way were collected and measured. The C_3–C_4 fractions were always analyzed by low-temperature distillation. The yields of iso-C_4 hydrocarbons obtained by this method are reported in grams per cubic meter of inert-free carbon monoxide-hydrogen mixture.

A quantitative analysis of the oxygenated organic compounds present in the liquid-hydrocarbon fraction and in the reaction water was made with each determination of yields. The liquid-hydrocarbon fraction was subjected to precise fractional distillation. In such cases, synthesis experiments were carried out on a somewhat larger scale to obtain enough liquid reaction products.

DESCRIPTION OF TECHNIQUES

GAS ANALYSIS

Gases were determined individually rather than in the Orsat apparatus. When no dimethylether was present, carbon dioxide was removed, and then the so-called heavy hydrocarbons were extracted, generally with fuming sulfuric acid. Under the same reaction conditions, and especially for the same reaction time, this method gives comparable results. It should be remembered, however, that in addition to unsaturated or aromatic hydrocarbons, the gases may contain branched compounds, also, which undergo alkylation and other reactions. Where the gas-analysis data were intended for subsequent calculations, the olefin content was determined with mercury nitrate. When necessary, iso-butene was first removed with 64 percent sulfuric acid. Oxygen and carbon monoxide were measured by the customary procedure, using pyrogallol and an ammoniacal solution of cuprous chloride. Hydrogen was burned over copper oxide at 250° C. Similarly, the hydrocarbons were mixed with oxygen and heated in a second converter to a bright red over a copper oxide-pumice catalyst. The amount of saturated hydrocarbons and their average carbon number were determined from the contraction and from the quantities of carbon dioxide formed during combustion. Nitrogen was calculated by difference. In addition, the nitrogen content of the inlet and outlet gas was always determined in order to permit calculation of the contraction occurring during synthesis. In these determinations, the whole gas was burned in oxygen after removal of the carbon dioxide. The results of the nitrogen determinations were the basis for the complete product analyses, because accurate calculation of contraction values was important for the balance sheets.

DETERMINATION OF DIMETHYLETHER

In a number of experiments, the outlet gas was found to contain dimethylether (b. p. −24.9° C.). When no special measures are introduced into the analytical procedure, this compound dissolves partly in sulfuric acid, giving rise to erroneous values for carbon dioxide and olefins. Dimethylether is relatively soluble in water (at 18° C., in an atmosphere of dimethylether, 37 liters of the ether dissolves in 1 liter of water.) However, when the gas contains only small amounts of dimethylether, an equilibrium between the gas phase and the solution establishes itself. As a result, to insure a sufficient degree of accuracy, the absorption pipettes, which contain water or a saturated solution of sodium chloride, must always be refilled. Dimethylether is considerably more soluble in concentrated sulfuric acid [24] (600 volumes to one), but this reagent

[24] Erlemeyer and Kriechbaumer: Ber. deutsch. chem. Gesell., vol. 7, 1874, p. 699.

cannot be used when olefins and branched hydrocarbons also must be determined.

The analytical procedure was the following: When dimethylether occurred in large amounts, carbon dioxide was first scrubbed from the gas with soda lime, a mercury seal being used. The dimethylether was then absorbed in pipettes filled with a sodium chloride solution. When dimethylether was present in only small amounts (a few tenths of a percent or less, by volume), it was determined by a separate process. For this purpose, a rather large quantity of outlet gas was bubbled directly from the synthesis unit, through a fritted-glass wash bottle filled with sulfuric acid, and then metered through a gasometer. The sulfuric acid containing the dimethylether was added dropwise to an equal volume of water contained in an evacuated flask that was connected by a small reflux condenser with a second evacuated flask of 5-liter capacity. The dilute sulfuric acid was boiled until the manometer connected with the system showed no further increase in pressure. The 5-liter flask was then sealed off from the reflux condenser, and volume of the gas collected in it was calculated from the pressure. For a more accurate determination of the dimethylether content of the flask, a known volume of gas was removed with a mercury burette, and the dimethylether was absorbed with concentrated sulfuric acid. Numerous trial experiments showed that both methods gave satisfactory results.

A third method consisted of the following procedure: After removal of carbon dioxide with soda lime, the outlet gas issuing from the reactor was cooled at very low temperature; dimethylether and the gasol hydrocarbons were separated as solids. As the receiver was carefully warmed, the gas was bubbled through a soda lime column, where all traces of carbon dioxide were removed, and then directly to the distilling flask of a low-temperature distillation column. During the subsequent precise distillation, the fractions containing dimethylether were collected in evacuated, calibrated flasks equipped with manometers. As a check, the dimethylether content of the individual fractions was also determined by the gas-analysis method of absorption with a solution of sodium chloride. Most of the dimethylether distilled over near its boiling point and was collected as a fraction intermediate between C_3 hydrocarbon and iso-butane.

STUDY OF THE GASOL FRACTION

For the determination of the gasol fraction (C_3–C_4 hydrocarbons), a quantity of 2 to 20 liters of the hydrocarbon product that was collected in the pressure trap of the syntheses system and in the activated charcoal trap (recovered from the latter by steaming) was condensed in the weighed flask of a low-temperature column,[25] which was cooled in an acetone-carbon dioxide snow mixture. Some n-pentane was added to insure complete distillation. The column [26] consisted of a glass spiral (6 meters of glass tubing coiled in a 1-meter column) contained in a silvered, evacuated jacket. The usual rate of distillation was 25 cc. of gas per minute. When passing from one plateau in the distillation curve to another, this rate decreased 50 percent. The fraction that distilled below −27° C. was the C_3 fraction. C_1 and C_2 hydrocarbons were collected at the column head as "forerunnings" during condensation and heating and were analyzed by standard gas-analysis methods and carbon-number determinations. The fraction distilling between −27° and −7° C. is the iso-butane fraction, and between −7° to 10° C. is residual C_4 fraction. Carbon numbers and the unsaturated contents were determined for all three fractions. For the C_3 fraction, the determination of unsaturated compounds was made with a mercury nitrate solution,[27] whereas in the other two fractions, iso-butane was first removed with 64 percent sulfuric acid, and the mercury nitrate determination was used for the remaining olefins. A typical qualitative indication of the presence of iso-butene is the yellow precipitate formed with mercury nitrate.

When distillation is complete, the flask is again weighed. In addition to the n-pentane added before distillation, it contains the C_5 hydrocarbon product fraction, which is determined separately.

DISTILLATION OF LIQUID HYDROCARBONS

The liquid hydrocarbon fraction was kept under refrigeration because of its high iso-pentane content. This fraction was freed from dissolved gasol by distillation up to a temperature of 20° C. through a large vacuum-jacketed, packed column. In preparation for the precise distillation, a sample quantity of a few liters of the stabilized product was mildly hydrogenated over a reduced precipitated nickel catalyst in a rotating autoclave at 500 atmospheres of hydrogen and a temperature of 100° to 150° C.[28] The saturated product was treated with ice water to remove any water-soluble alcohols.

[25] Carbon dioxide present in the hydrocarbon fraction was removed with potassium hydroxide, and water vapor was removed with calcium chloride.

[26] Koch, H., and Hilberath, F., work cited in footnote 17.

[27] Hurd, C. D., work cited in footnote 19.

[28] Whenever the liquid hydrocarbons were cooled in an atmosphere of hydrogen after hydrogenation, they were observed to contain small amounts of nickel carbonyl produced in the presence of traces of carbon monoxide in technical hydrogen. This carbonyl was difficult to remove quantitatively and proved to be a source of error in determining such values as the gasoline antiknock rating. Its formation can be prevented by removing the hydrogen at 100° C. at the end of the reaction and cooling the liquid product in the absence of hydrogen.

Sometimes it was further washed with concentrated hydrochloric acid to remove residual alcohols. Finally, it was dried, first over calcium chloride and then over sodium.

Three different columns were generally available for distilling the liquid product: (*a*) A glass-packed column placed within a silvered vacuum jacket. The packed tube had an inner diameter of 35 millimeters and was 1.6 meters long. For a distillation rate of one-half drop per second, the reflux ratio (of the material refluxing to the distillate) was 40:1. The column was used for 2 to 5 liters of starting material. (*b*) A column with a rotating band 30 centimeters long, of the type described by Koch, Hilberath, and Weinrotter.[29] This column was usually used to redistill 10 to 50 cc. of individual fractions from large-scale distillations. (*c*) A column of the type described in (*b*) but with a rotating band of 1 meter. The efficiency of this column corresponded to 36 theoretical plates. For a reflux ratio of 40:1, the rate of distillation was one drop per 40 seconds. The capacity of the column was 30 to 500 cc.

DETERMINATION OF UNSATURATED LIQUID HYDROCARBONS

Under the conditions of the isosynthesis, the products contained 10 to 60 percent of unsaturated compounds. The unsaturated content was measured by iodine number determinations of the total product, and the individual fractions were obtained by a special precise distillation of the unhydrogenated product. The iodine-thiocyanate method of Kaufmann and Grosse-Oetringhaus [30] was used. As Koch and Hilberath [31] have shown, this method is particularly useful for mineral-oil products, because it reduces the possibility of substitution errors in the presence of branched hydrocarbons.

DETERMINATION OF AROMATIC COMPOUNDS

In order to avoid errors due to alkylation and other reactions, sulfuric acid was not used in determining aromatic compounds. The aromatic content was determined by the method of Grosse and Wackher,[32] which was based upon the observation that specific dispersion $(n_F - n_{C/d})n$ 1,000 is approximately 190 for aromatic compounds and 99 for naphthenes and paraffins boiling in the gasoline range, irrespective of their constitution. Allowing for the olefin content, the relation is as follows:

$$\text{Weight percent aromatics} = \left(\frac{\Delta \text{ mixture} - (0.16 \text{ bromine no.}) - 99}{\Delta \text{ aromatics} - 99}\right)100$$

where "Δ mixture" is the dispersion of the mixture, as defined above, and "Δ aromatics" is the dispersion of the aromatic hydrocarbons whose boiling points fall within the range of the fraction under consideration.

To analyze its aromatic content, the crude isosynthesis product was separated into the following fractions by distillation in a glass spiral column [33] (length of spiral, 1 meter; length of tube, 6 meters):

Fraction:	° C.
1	<65
2	65–95 (benzene)
3	95–125 (toluene)
4	125–150 (xylene)
5	150–175 (C_9–C_{10})
6	175–200 (C_{10}–C_{11})

The values of "Δ aromatic" of the above fractions are known; they range from 190.2 for benzene to approximately 171 for the C_{10}–C_{11} fraction. An Abbé refractometer was used to determine the dispersion for the individual fractions.

In certain experiments (for example, from aluminum oxide-chromium oxide catalyst at 500° C.), the liquid hydrocarbon fraction was chiefly aromatic. In such cases, the fraction that boiled in the gasoline range was separated by distillation and analyzed directly.

Of the aromatic hydrocarbons identified, hexamethyl benzene (m. p. 165° C.) frequently occurred in relatively large amounts. The compound was purified by recrystallization from benzene or alcohol.

DETERMINATION OF ACIDS, ESTERS, ALCOHOLS, ALDEHYDES, KETONES, AND PHENOLS

The amounts of acids and esters formed by isosynthesis are extremely small. Under certain conditions, usually not very favorable to hydrocarbon formation, alcohols, especially methanol and isobutyl alcohol, were obtained in appreciable amounts. Phenols occurred only in a single instance (an alkalized catalyst, 500° C.).

The acid and ester numbers of the reaction products were determined by the usual methods. Alcohols were determined from the acetylation number [34] calculated for an average experimental value of the molecular weights. Quantitative determination of the water-soluble

[29] Koch, H., Hilberath, F., and Weinrotter, F., [A Column with Rotating Metal Band for the Fractional Distillation of Small Amounts of Substances]: Chem. Fabr., vol. 14, 1941, pp. 387–390.

[30] Kaufmann, H. P., and Grosse-Oetringhaus, H., [Quantitative Determination of Unsaturated Hydrocarbons in Mixtures]: Ber. deutsch. chem. Gesell., vol. 70, 1937, pp. 911–915.

[31] Koch, H., and Hilberath, F., [Investigation of the Methods of Determining Iodine Numbers of Hydrocarbons]: Brennstoff Chem., vol. 21, 1940, pp. 185–193.

[32] Grosse, A. V., and Wackher, R. C., Quantitative Determination of Aromatic Hydrocarbons by New Method: Ind. Eng. Chem., anal. ed., vol. 11, 1939, pp. 614–624.

[33] Jantzen, E., [Fractional Distillation and Fractional Separation as Methods of Analyzing Mixtures]: Dechema-Monographie, No. 48, Bd. 5, 1932.

[34] Verley and Bölsing: Ber. deutsch. chem. Gesell., vol. 34, 1901, p. 3354. Wolff, H.: Chem. Umschau, vol. 1922, p. 1.