FIAT FINAL REPORT NO. 276

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KAISER WILHELM INSTITUT FUER KOHLENFORSCHUNG. MUELHEIM, RUHR. INTERROGATION OF DR. HELMUTH PICHLER AND PROF. KARL ZIEGLER

Margaret Horne

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KAISER WILHELM INSTITUT FUER KOHLENFORSCHUNG
MUELHEIM, RUHR
INTERROGATION OF
DR. HELMUTH PICHLER AND PROF. KARL ZIEGLER

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Technical Industrial Intelligence Committee

FIELD INFORMATION AGENCY, TECHNICAL

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INTERROGATION OF DR. HELMUT PICHLER AND PROFESSOR KARL ZIEGLER AT THE KAISER WILHELM INSTITUTE FÜR KOHLENFORSCHUNG MULHEIM, RUHR.

Introduction.

This target was revisited to obtain further information concerning "Isosynthesis" and the results of the comparative tests on iron Fischer-Tropsch catalysts conducted at Schwarzheide-Ruhland.

The information presented herein is in addition to and supplements that previously reported in the C.I.O.S. report dated 15 June 1945, "Kaiser Wilhelm Institute für Kohlenforschung, Mulheim, Ruhr", by Dr. V. Haensel (PAW., U.S.).

ISOSYNTHESIS.

1. Summary.

In the so-called "isosynthesis", carbon monoxide and hydrogen are converted predominantly to branched hydrocarbons by oxide catalysts. Similarly to the normal or medium-pressure synthesis, isosynthesis results in the production of hydrocarbons from methane to those of high molecular weight. In isosynthesis, however, the principal products are isobutane and the low-boiling hydrocarbons of gasoline. Although in normal-pressure and medium-pressure synthesis, less than 10% of the C_4 hydrocarbons are branched, this fraction from isosynthesis contains 90% of iso C_4 compounds. The liquid hydrocarbons (above C_4) from isosynthesis contain about 30% of isopentane. Among the compounds boiling above 100°C., increasing proportions of naphthenes are present (especially when the operation is conducted at temperatures above 450°C). Considerable proportions of aromatic hydrocarbons are formed at temperatures above 500°C.

2. Catalysts.

Thoria was found to be a particularly good catalyst. It can be improved by the addition of alumina particularly if the production of isobutane is desired. If the formation

of liquid hydrocarbons is preferred, at the expense of the C_4 fraction, it is necessary to add small proportions of alkali to the catalyst. In place of thoria, other metal oxides were used, such as zirconium oxide and, with less success, ceria.

Thorium oxide can be replaced partially by mixed catalysts. A combination of zinc oxide and alumina was found to be good. The permissable charging rates are, however, smaller for these catalysts than for the basic thoria catalyst.

Thoria catalysts were usually precipitated by soda from nitrate solutions, with the practice of pouring rapidly the boiling soda solution into the boiling nitrate solution. In this way, for example, by using concentrations of 240 g. of thorium nitrate in 2 liters of water and 2 liters of soda solution (containing a small excess of sodium carbonate), a hard granular catalyst is obtained after washing the precipitate free from alkali and drying at 110°C. (apparent density 1.3). If concentrated solutions are used, catalysts of low apparent density are produced that are not strong physically. Less active catalysts that are very hard and give a vitreous fracture are made if the mixture of the solutions is made slowly (e.g. in one hour). B, precipitating with sodium hydroxide or ammonia, inferior catalysts are produced even by rapid mixing (apparent density 2.3). The apparent density can be increased in each case by sintering in a stream of air. A normal catalyst was raised in apparent density from 1.3 to 2.0 by heating in air at 300°C. (*) The catalyst remains dull in appearance and hard.

Since a catalyst dried at 110°C. shrinks during the synthesis, it is advantageous to carry out the sintering before charging the catalyst. Up to 300°C., shrinkage results from loss of water and carbon dioxide. At higher

(*) Alkali metal carbonates precipitate basic salts from solutions of thorium nitrate, with evolution of carbon dioxide. By heating at 240°C, $ThO\ CO_3\ 2\ H_2O$ is changed to $3\ ThO_2\ ThO\ CO_3\ H_2O$. This compound is then changed to $4\ ThO_2\ H_2O$ at 300°, and at higher temperatures (above 400°C) to ThO_2.

temperatures, firmly bound water is driven off without further shrinkage of the catalyst or lowering of its activity. On the contrary, a thorium catalyst heated to 1000°C. in air, showed an especially good converting power for synthesis gas. Since such a catalyst caused a somewhat increased production of methane, calcining was limited to 300°C.

For the preparation of a mixed thoria-alumina catalyst, it was found to be advantageous to precipitate the oxides separately: thoria from its nitrate solution by sodium carbonate, and alumina from sodium aluminate by acid; e.g. sulfuric acid. After washing, the two oxides are mixed thoroughly and dried. The preparation of a 20% alumina - 80% thoria catalyst is prepared as follows: Two hundred and forty grams of thorium nitrate dissolved in two liters of distilled water is heated to boiling and precipitated (as explained) by a boiling solution of 95 g. of sodium carbonate in two liters of water. The filtered precipitate is washed fifteen times with 400 cc batches of boiling water. Separately, 169 g. of aluminum nitrate dissolved in a liter of water and mixed while boiling with 77 g. of sodium hydroxide dissolved in 500 cc of water (the aluminum hydroxide first precipitated dissolves, the solution being only slightly turbid). Alumina is precipitated by adding to the boiling solution 17.2 cc of concentrated sulfuric acid in 350 cc of distilled water. This precipitate is washed twelve times by suspending it each time in 1 liter of water, settling and decanting. It is then separated on a suction filter, and washed three times with 400 cc lots of boiling distilled water.

The two precipitates are mixed well and suspended in hot water, evaporated down on a water bath with constant stirring and then dried at 110°C. and calcined in air at 300°C.

Catalysts used in isosynthesis were regenerated from time to time by passing air over them at the temperature of the synthesis. The time between regeneration varies, depending upon the rate of formation of carbon (usually after several weeks). Activity was not impaired by regeneration with air. The catalyst is not sensitive to sulfur compounds.

3. Operating Conditions.

a) Pressure of the Isosynthesis.

At a pressure of one atmosphere, carbon monoxide and hydrogen do not react when passed over the catalysts of isosynthesis. If the pressure is raised slightly, a small reaction is detectable, and becomes appreciable at 50-100 atm. The best pressures are in the range of 300-500 atm. At higher pressures than these, the proportion of oxygenated derivatives becomes appreciable. Dimethyl ether becomes a main product for example at pressures above 1000 atm.

b) Temperature of the Isosynthesis.

The optimum temperature lies between 400 and 450°C. At higher temperatures, objectionable cracking sets in, and increasing proportions of methane are formed. Below 400°C., the liquid fractions contain considerable proportions of alcohols, especially of isobutyl alcohol and methanol.

c) Synthesis Gas.

Technical water gas is used. The best yields are obtained with a $CO:H_2$ ratio of 1.0-1.2:1.0. Special purification of the gas is not necessary. In order, however, to prevent carbonyls formed in the high-pressure storage vessels (3000 atm) from reaching the reaction vessels, the gas is led through an active carbon adsorber.

d) Space Velocity.

In most of the experiments, water gas was fed at a rate of 15-20 liters per hour for each 25 g. of thoria in the catalyst used (about 10 liters of exit gas). For a liter of catalyst, the hourly rate of synthesis gas is of the order of 1000 liters.

4. Converter.

Tubes of 15-50 mm. internal diameter (usually 20 to 25 mm) are used. If larger tubes are used, it is advantageous to insert co-axially a perforated inner tube in order to insure better distribution of the feed, the catalyst filling the annular space. (German patent 708,500 describes the arrangement).

The tubes as well as the attached lines are sheathed with sheet copper in order to prevent the formation of carbonyl and excessive proportions of methane. Up to a certain extent, copper lining can be avoided by using high alloy steel tubing.

Isosynthesis is not as sensitive to temperature change as are the normal pressure and the medium pressure synthesis. Nevertheless, when working on a large scale, ample provision must be made for removing the strongly positive heat of reaction to maintain a uniform temperature.

Steel tubes were used generally on the laboratory work. Temperature control was effected by using aluminum-block furnaces, well-known from the work on normal pressure synthesis. For larger scale work, the tubes can be put into baths of molten salts. The laboratory apparatus employed is shown in Figure I.

5. Yield.

Table I presents yields that were obtained by using a series of thoria catalysts at 450°C. and 300 atm. single pass. In all runs, the out-gas rate was 10 liters per hour per 28 g. of thoria.

The experiments summarized in the table give an indication of the variability of the isosynthesis process. These variations can be increased still further by changing pressure and temperature. For example, experiment 3 of the table gives, at 600 atm. for a CO conversion of 82%, the following products:

Liquid Oil	56 g.
Alcohols	1 g. in the oil,
	3 g. in water
Iso C_4 hydrocarbons	61 g.
n-Butane	7 g.
C_3 Hydrocarbons	5 g.
C_2 Hydrocarbons	5 g.
Methane	7 g.
Dimethyl ether	8 g.

At temperatures below 400 C., almost 100% of alcohols was obtained with a thoria-zinc oxide catalyst. The composition of the liquid hydrocarbons can also be varied. At the

lower reaction temperatures, relatively more high boiling products are formed.

In a run over a thoria-alumina catalyst at 300 atm. and 450°C., the liquid hydrocarbons consisted of roughly 30% isopentane, 20% branched aliphatic C_6 hydrocarbons, 10% isomeric heptanes, 5% octanes etc. About 20% was variously alkylated naphthenes and 10% was undetermined hydrocarbons that, especially at low reaction temperatures, have the general character of lubricating oils.

6. Procedure.

The dried sintered catalyst is put into the tube and the gas pressure and rate are established. The temperature of the furnace is then brought to the desired level. The extent of conversion is checked periodically by gas analysis. Most of the oil is separated in the condenser and the remainder is recovered from the activated carbon adsorbers. Gasol (recovered from adsorbers), liquid oils and alcohols were separated by close distillation and characterized.

7. Mechanism of the Reaction.

Contrary to the conclusions about the ordinary pressure and medium pressure synthesis, oxygenated compounds, especially alcohols and ethers, can be assumed to be intermediate products of isosynthesis. The composition of the branched chain hydrocarbons in the fractions does not correspond to equilibrium conditions; formation of the branched compounds, therefore, from the straight chain hydrocarbons seems to be precluded. The compositions of the alcohols does not make it seem probable that all the hydrocarbons are formed from alcohols. It is, however, probable that isobutyl alcohol, dimethyl ether and isobutane play the role of intermediates. By starting with a mixture of dimethyl ether and hydrogen, similar products are formed by thoria as from water gas. Thoria alone, therefore, is capable of forming primarily alcohols and ether, to dehydrate these compounds to unsaturated branched chain hydrocarbons, especially isobutene, and to transform these unsaturated compounds by polymerization, alkylation, isomatization and hydrogenation.

TABLE I.

YIELDS FROM VARIOUS THORIA CATALYSTS AT 300 ATM AND 450°C.

Experiment No.	Catalyst	% CO converted.	Yield in Gms per N.cu.m. $CO-H_2$ Mixture							
			Liquid Hydrocarbons	Alcohol oil.	In H_2O	iC_4	nC_4	C_3	C_2	C_1
1.	ThO_2	62	42	9	11	23	3	11	4	11
2.	ThO_2 + 0.6% K_2CO_3	62	65	21	5	12	1	8	1	6
3.	ThO_2 + 20% Al_2O_3	73	34	1	2	61	9	9	10	15
4.	ThO_2 + 20% Al_2O_3 + 3% K_2CO_3 (based on Al_2O_3)	78	25	0	0	85	10	0	7	22
5.	ThO_2 + 20% Al_2O_3 + 0.6% K_2CO_3 (based on ThO_2)	70	42	2	4	51	7	18	6	12

COMPARATIVE EXPERIMENTS WITH IRON CATALYSTS IN MEDIUM PRESSURE SYNTHESIS.

The object of a series of experiments made in 1942-43 at the plant of the Braunkohlen-Benzin A.G., (Schwarzheide-Ruhland) was to enable a group of companies to arrive at the best possible catalyst for the iron catalyst medium pressure synthesis developed in the Kaiser Wilhelm Institute für Kohlenforschung, Mulheim-Ruhr. Six firms submitted their iron catalysts that had been prepared by different methods, different shaping and different pretreatments prior to the actual synthesis.

The results obtained with the converter operated at Ruhland by members of the Institute, as well as a tabulated summary of the results obtained with the other participants' converters, is presented here.

The conditions set for each participant were as follows:-

(1) Highest permissable temperature of synthesis, 225°C.

(2) Pressure of synthesis, 10 atm.

(3) Catalyst volume of the converters (all converters of the same type), 4.8 l.

(4) Synthesis gas, technical water gas.

(5) Period of operation (uninterrupted), 3 months.

All these conditions were observed by the participants.

The catalyst used by the Kaiser Wilhelm Institute was prepared in the following usual way: The iron was precipitated from the boiling dilute nitrate solution by the boiling soda solution. One per cent of copper (based on the iron) had been added to the iron solution before precipitation. The precipitate was filtered and washed with hot distilled water until free from alkali. A paste was then made with distilled water and a solution of potassium carbonate (containing 1% of potassium carbonate, based on the iron) is mixed with the paste. Thickening of

the paste is effected on a waterbath and drying completed at 105°C. in an oven. The dried pieces are then broken into granules of 2-4 mm.

The pretreatment of the catalyst was as follows:-

A mixed gas, rich in hydrogen (CO:H = 1:2), was passed over the catalyst for 24 hours, at a pressure of 0.1 atm. and a temperature of 325°C., (8 liters of gas per hour per 10 g. of iron). The strongly pyrophoric catalyst was then soaked in paraffin wax toprotect it from oxidation, and put into the converter with as little contact with air as possible.

At the beginning of the synthesis, the catalyst was very active at 185-190°C.

In order to maintain the percentage of conversion throughout the 3-month test, the temperature was raised gradually from 195-224°, for the most part between 215-220°C.

Average results over the period are given below for the Kaiser Wilhelm Institute converter:-

Composition of the charged, technical water gas:

CO_2	CO	H_2	CH_4	N_2
6.2	39.2	48.8	2.6	3.2

Contraction of the gas volume by synthesis 42.5%
CO conversion 85.0%
Total yield of products (including methane) ..... 125.2 g.per normal cu.m. of water gas (above composition).

Analysis of Products:

Gas (C_1 + C_2)	20.8	g/N	cu.m.
Gasol (C_3 + C_4)	24.9	"	"
Gasoline (C_5 - C_{10})	31.4	"	"
Diesel Oil (C_{11} - C_{18})	17.6	"	"
Paraffin (Gatsch, boiling 320-450°)	9.9	"	"
Hard Wax (boiling above 450°C)	12.9	"	"
Lower Alcohols	7.7	"	"
	125.2	"	"

The attached Table II gives a summary of the results (single pass) obtained with the six converters of the participants.

Converter 1. Kaiser Wilhelm Institute für Kohlenforschung, Mulheim.
2. Lurgi Gesellschaft für Warmetechnik, Frankfurt.
3. Braunkohle-Benzin A.G., Ruhland-Schwarzheide.
4. I.G.Farbenindustrie A.G., Ludwigshafen.
5. Ruhrchemie, A.G., Oberhausen.
6. Rheinpreussen, Homberg, Ruhr.

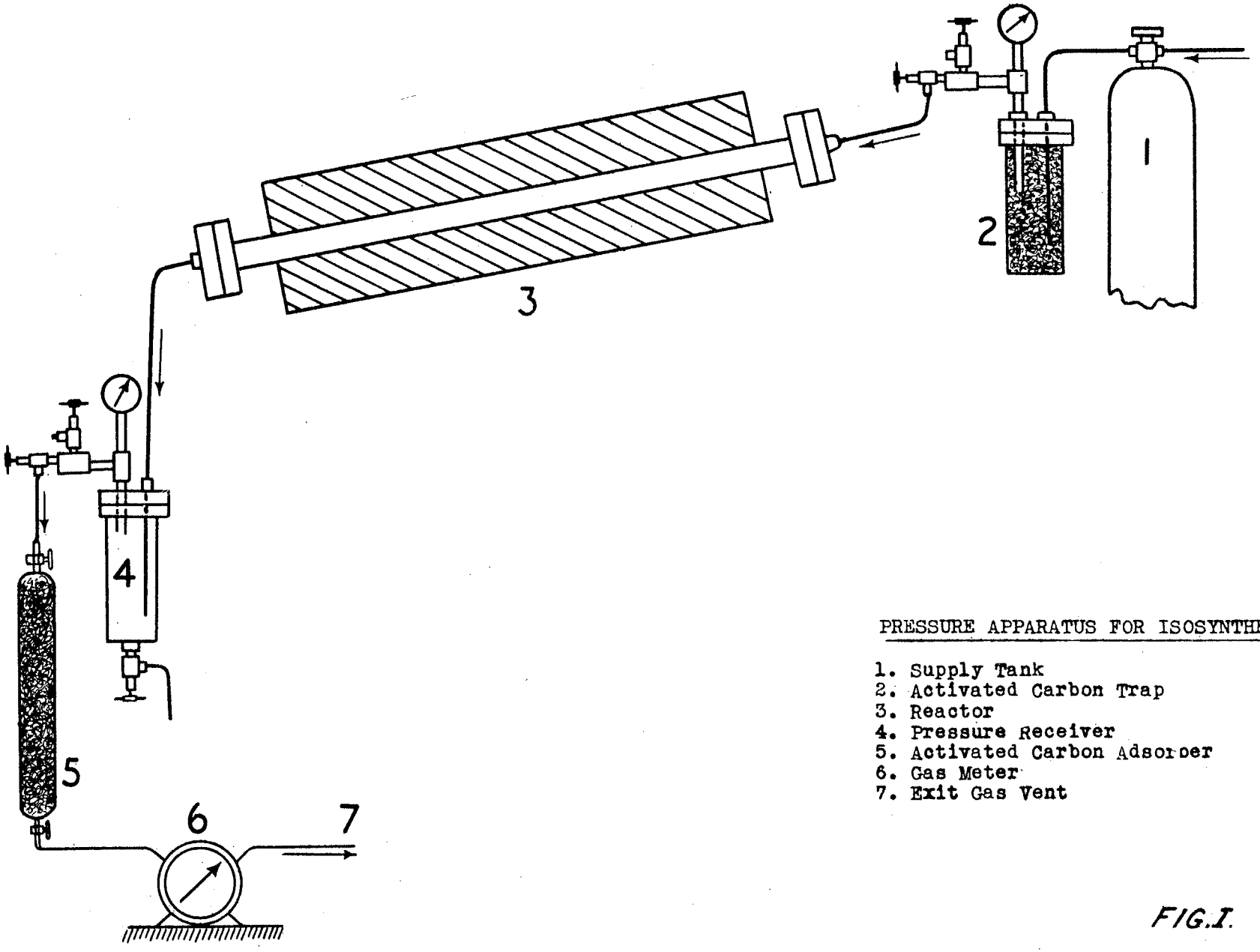
The yield of a given carbon number fraction is shown in metric tons per day, the quantity of product that the 10 cu.m. (catalyst volume) converter of the industry would make in 24 hours. The percent unsaturation of the fraction is also shown.

The alcohols are shown in two fractions, the first (lower boiling) was recovered from the reaction water, and the second (higher boiling) recovered from the oil product. The second fraction consists principally of alcohols above butyl alcohol.

TABLE II.

COMPARATIVE RESULTS OF MEDIUM PRESSURE SYNTHESIS. SINGLE PASS USING IRON CATALYSTS RUHLAND SCHWARZHEIDE.

Fraction	KWI		LURGI		BBS		IGF		RCH		RHPR	
	T/D yld	% unsat.	Yld. T/D	Unsat. %	Yld. T/D	Unsat. %	Yld. T/D	Unsat. %	Yld. T/D	Unsat. %	Yield T/D	Unsats %
C_1	0.26	-	0.18	-	0.11	-	0.29	-	0.18	-	0.21	-
C_2	.29	10	.17	53	.12	51	.25	39	.17	36	.23	10
C_3	.37	53	.20	67	.15	79	.34	77	.21	70	.31	54
C_4	.28	50	.19	66	.15	79	.26	65	.16	53	.25	56
C_5	.19	64	.16	65	.10	73	.21	70	.12	61	.19	59
C_6	.16	56	.11	57	.10	73	.15	66	.11	57	.15	54
C_7	.13	49	.08	58	.08	73	.13	64	.08	53	.12	51
C_8	.11	44	.08	60	.06	67	.11	64	.07	46	.11	49
C_9	.09	41	.04	60	.06	74	.07	64	.05	45	.09	46
C_{10}	.09	32	.05	63	.07	74	.08	65	.05	48	.08	41
$C_{11/12}$	.13	24	.08	63	.09	71	.09	62	.08	39	.10	33
$C_{13/14}$	.12	17	.09	59	.10	73	.08	58	.06	33	.09	19
$C_{15/16}$	.10	10	.07	54	.09	51	.07	54	.05	31	.09	14
$C_{17/18}$	.09	5	.05	47	.09	46	.06	44	.05	25	.06	10
Gatsch	.26	3	.21	29	.31	26	.19	32	.16	17	.15	7
Hard Par.	.32	-	.72	13	.82	8	.44	7	.45	7	.16	-
Total Hcs. Lower	2.99		2.48		2.50		2.82		2.05		2.39	
Alcls	0.20		0.28		0.13		0.13		0.16		0.06	
Higher	0.04		0.18		.11		.05		.07		0.01	
Esters	0.03		0.25		.12		.23		.29		0.14	
Total oxygen compds	0.27		0.71		0.36		0.41		0.52		0.21	



PRESSURE APPARATUS FOR ISOSYNTHESIS

1. Supply Tank
2. Activated Carbon Trap
3. Reactor
4. Pressure Receiver
5. Activated Carbon Adsorber
6. Gas Meter
7. Exit Gas Vent

FIG. I.

25-80308-450