Mines Branch Information Circular IC 229

OILS AND BASIC ORGANIC CHEMICALS FROM COAL BY HYDROGENATION
(A LITERATURE REVIEW)

by

W.A.O. Herrmann*

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ABSTRACT

The literature published since World War II on coal hydrogenation and its economics, and on the production of chemicals from coal, is critically reviewed. The advantages and disadvantages of different operating schemes are discussed from the viewpoint of the author's own experience as far back as 1936 in German coal hydrogenation plants. Some possibilities of improvement and cost savings are discussed. The feasibility of extracting basic chemicals from the products of coal hydrogenation and of converting such by-products to basic chemicals of higher value is considered, as well as the contribution of such an operation towards improving the economics of coal hydrogenation.

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Direction des mines

Circulaire d'information IC 229

HUILES ET PRODUITS CHIMIQUES ORGANIQUES DE BASE PROVENANT DU CHARBON PAR HYDROGÉNATION

(REVUE DE PUBLICATIONS)

par

W.A.O. Herrmann*

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RÉSUMÉ

L'auteur passe en revue d'une manière critique les publications, parues depuis la Seconde Guerre Mondiale, sur l'hydrogénation du charbon et son aspect économique, ainsi que sur la production de produits chimiques à partir du charbon. Les avantages et désavantages de différents modes d'exploitation sont analysés du point de vue de l'expérience personnelle de l'auteur remontant à 1936, dans des usines d'hydrogénation du charbon en Allemagne. Des possibilités d'amélioration et de réduction des frais sont discutées. La possibilité d'extraire des produits chimiques fondamentaux, à partir des produits de l'hydrogénation du charbon, et aussi de convertir de tels sous-produits en des produits chimiques fondamentaux de valeur plus grande, est considérée, de même que la contribution d'une telle opération vers l'amélioration des conditions économiques de l'hydrogénation du charbon.

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INTRODUCTION

The reason for the current renewal of interest in coal hydrogenation in North America is an anticipation of a change in the pattern of energy consumption and supply. Up to the time of the first World War, coal provided, in North America and in Europe (with exception of Norway), almost all of the energy required for industrial and domestic use. The increase in the number of motor vehicles after World War I, however, led to the rapid development and expansion of the petroleum industry, especially in North America.

By the end of the second World War the basic organic chemical industries, especially those of plastics and rubber, had expanded so much and so rapidly that raw materials like phenol, aromatics and olefines could no longer be supplied in sufficient quantity by the coal-tar industry; thus, chemicals derived from petroleum appeared to provide the obvious solution to this problem. This development was furthered by the continuing increase in crude-oil production and refining capacity and also by a shift in gasoline quality towards higher octane ratings. This in turn forced the aromatisation of the higher-boiling fractions of the gasoline and was associated with a higher production of unsaturated hydrocarbon gases. This development is illustrated in Table 1(1) which shows the estimated consumption of petroleum products in West Germany, and in Table 2, a comparison of the percentage consumption of refining products in the U.S.A. and West Germany, which shows that in the U.S.A. the relative gasoline production is about three times as great as in West Germany. Figure 1 illustrates the development of USA production of starting materials for organic chemicals from 1955.(18)

It is generally thought that hydrogenation is too expensive to produce motor fuels from coal. But our experience during World War II has shown that this opinion can change drastically, since it depends on the difference in the cost of energy of petroleum as compared with coal. The costs of coal hydrogenation can be further changed advantageously by incorporating some of the improvements developed after the war, and by producing a larger percentage of the higher-priced basic chemicals instead of low-priced fuels.

TABLE 1

Consumption of Petroleum Refinery Products in West Germany (in Million Tons per Year) (1)

	1966 (actual)	1970 (estimate)	1975 (estimate)
Crude gasoline for:			
Petrochemicals	3.7	7.8	10.7
Peak gas production	0.6	0.8	0.5
Solvents	0.3	0.3	0.3
Motor gasoline	11.6	15.8	19.7
Total gasoline	16.2	24.7	31.2
Turbine fuel	0.8	1.8	3.4
Diesel fuel	8.7	10.0	11.5
Light fuel oil	26.6	34.0	40.0
Heavy fuel oil	25.9	29.7	35.7
Others	9.0	10.8	13.5
Total consumption	87.2	110.0	135.3
Per capita consumption (ca)	1.56 tons	1.79 tons	2.06 tons
Motor gasoline, % of total	13.3%	14.3%	14.6%

TABLE 2

Percentage Consumption of Petroleum Refinery Products in the USA and in West Germany (1966) (1)

	USA	W. Germany
Motor gasoline	46	15
Raw gasoline	-	3
Middle distillates	32	44
Heavy fuel oil	8	25
Others	14	13

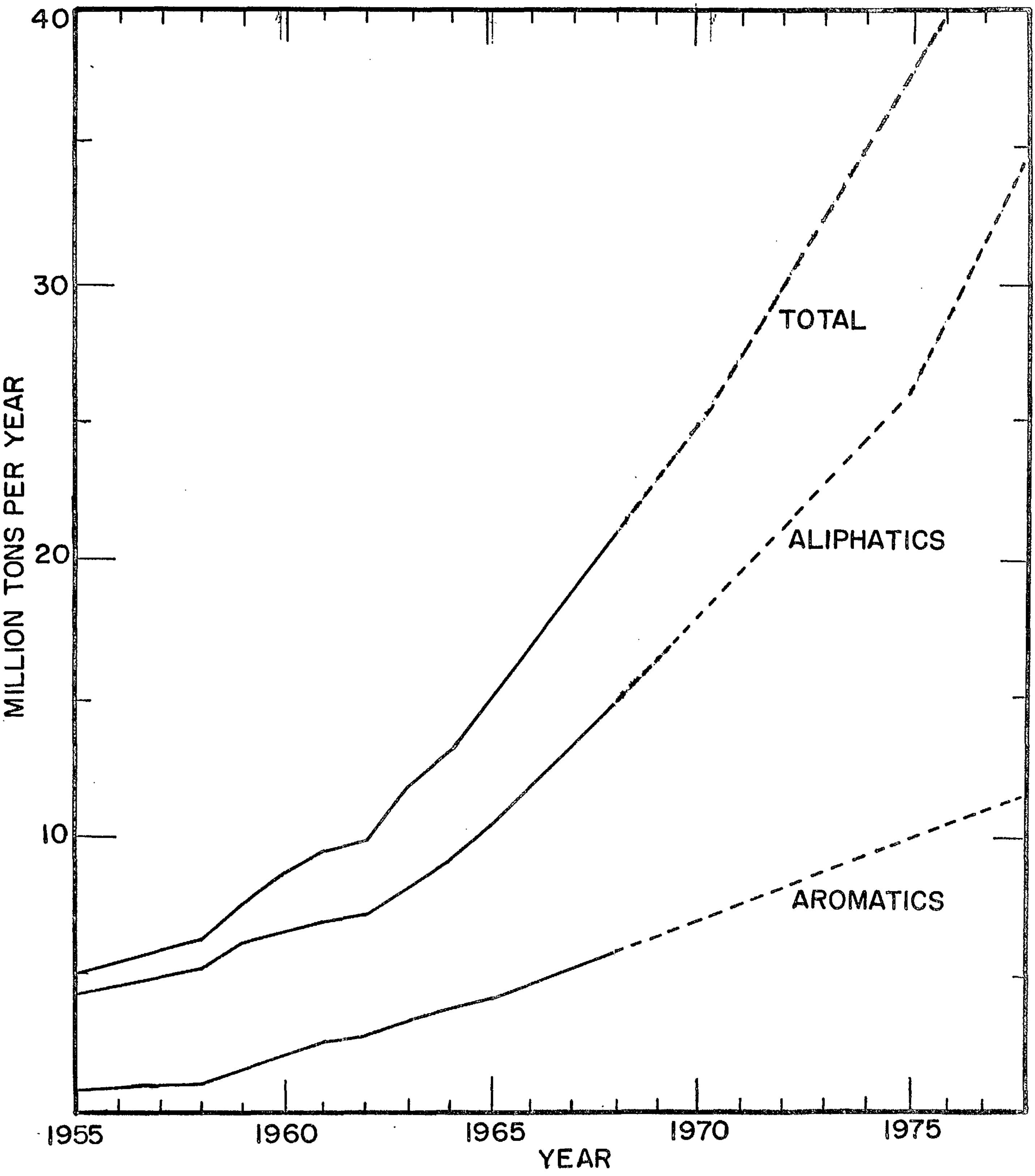

Figure 1. Development of USA production of starting materials for organic chemicals (from 1955).(18)

The purpose of the present survey was twofold: (a) to investigate some possibilities of producing basic organic chemicals from coal by hydrogenation, and (b) to compare the economic influences on the costs of such an operation relative to their production from petroleum.

CHANGES IN RAW MATERIAL RESERVES

In Canada the total consumption of energy in 1966 was made up of 10.4% by hydroelectricity, 15.1% by coal, 54.5% by petroleum products, and 18.4% by gas(2). The consumption of coal, which was 47 million tons in 1948, receded to 22 million tons in 1962, but has since risen to 26.3 million tons in 1967. The recoverable coal reserves are 30,544 million tons of bituminous and subbituminous coal and 12,122 million tons of lignite, representing an equivalent of 43,449 million tons of coal having a heating value of six million kcal per ton(3). At the present rate of consumption these reserves would last for about 1,620 years. The known Canadian oil reserves, not counting the oil sand and black pool deposits, would last, at the present consumption rate, for about 24 years. Present indications are that the rate of discovery, as compared with the rate of consumption, will increase for some time to come*. If the oil sands are included the reserves would last for 1,130 years. Although new reserves are currently being discovered at a rate greater than the consumption, the costs of exploration have gone up 2.3%, from 39.4¢/bbl in 1964 to 40.3¢/bbl in 1966.

In the United States the pattern is not very different. The known reserves of oil, not considering the shale-oil deposits, would last, however, only for about 11 years(3a) and the natural gas reserves for about 16 years, both showing a tendency to decrease, in spite of rising imports. It is estimated that during the next decade the annual petroleum consumption in the U.S.A. will increase by about 40%. In contrast to this, the known coal reserves are estimated to last much longer: at the rate of consumption in

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* The percent growth rate of the oil reserves from 1958 to 1966 has been 12.0%, while the growth rate of oil consumption was 10.2% in the same period. For natural gas the corresponding figures were 8.1% and 17.7%.

1965 in the U.S.A., for about 5,230 years; and in West Germany, for about 1,042 years.

The coal production in India was in 1952, according to M.N. Saha(4), 35 million tons per year, of which only 8.5% was used for domestic heating. Of a total energy consumption equivalent to 125 million tons per year, 66.5% was supplied by wood and cattle dung, and 5.6% by imported oil and hydroelectricity. If it is arbitrarily assumed that 1) the total energy consumption will rise in the future by only 1% annually, 2) the coal consumption by industry and transportation will increase by 1.5% annually, 3) the oil imports or domestic production will increase by 1% annually, and 4) at the same time the supply of wood and cattle dung for domestic heating is being replaced at a rate of 1% annually by coal or coke, the net result is an increase in the over-all consumption of 2.8% per year. This would mean that the 11 billion tons of coal deposits in India will be exhausted in about 44 years unless other ways to supply the required energy are found.

PRICES OF RAW MATERIALS AND THEIR CHANGES SINCE 1950

The oil reserves of the world in general, and of North America in particular, relative to the rate of consumption, will not increase forever. Even at present, increasing expenditures for explorations and processing of crudes, which will have a higher specific gravity and sulphur content, can be noticed. Although the price of crude at wellhead has decreased from 1958 to 1966 by 2.5%, the price of refined petroleum products has increased in the same period by the same 2.5%(5)

The price of coal in Canada per 10 million kcal has risen from $4.06 in 1958 to $6.41 in 1964, while in the U.S.A., due to increasing mechanization of the mines, the coal price has risen from $3.75 in 1955 only to $4.02. Figure 2 illustrates the development of the prices for coal and oil in $ per 10 million kcal in West Germany relative to North America since about 1954. It can be seen that in Western Europe the unit heat in coal costs about one and a half times as much as with oil. This complete reversal of the price ratio coal-versus-oil in Western Europe forced the cessation of the coal hydrogenation activities which had been resumed after the war.

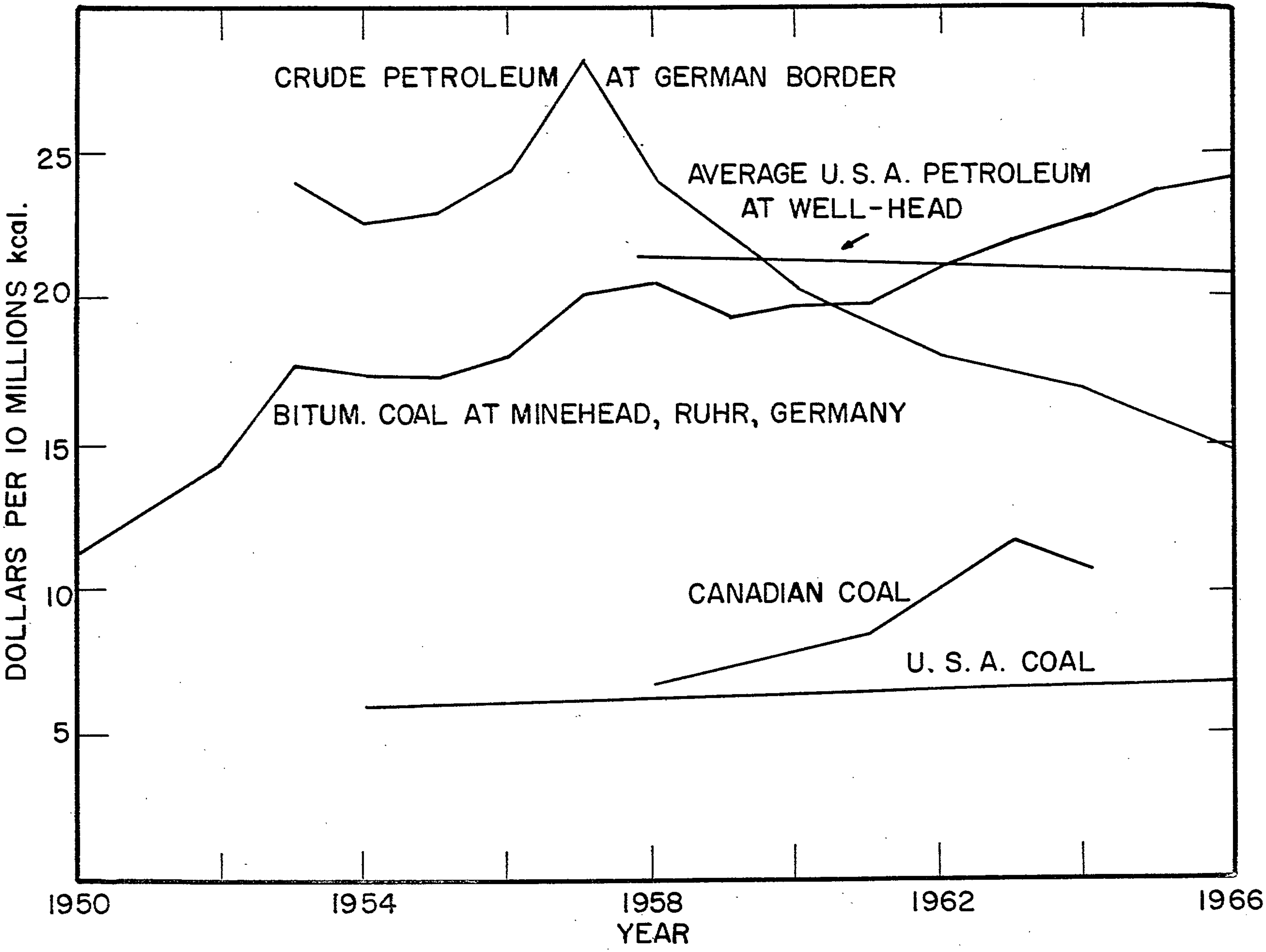

Figure 2. Prices for bituminous coal and crude oil in West Germany and North America, 1952-1966.(1)

Also, for chemical processes which are based on coal as raw material -- for example, the production of calcium carbide-acetylene -- the high coal price became prohibitive and these processes were largely replaced by petrochemicals. Even the hydrogenation of petroleum residues became unattractive, since they could be sold directly as replacement for the more expensive coal. Contrary to the development in Europe, the unit heat with oil in North America still costs about three times as much as with coal: per 10 million kcal, $22.10 versus $6.70 for coal. This price difference and the increasing costs to produce and process the petroleum provide the incentive to consider coal as an alternative raw material for the production of liquid fuels and chemicals. Therefore the large oil companies in the U.S.A. are acquiring coal fields and investigating improved methods of coal hydrogenation.

THE HIGH-PRESSURE HYDROGENATION OF COAL

1. Development

Right after the first World War the I.G. Farben experimented with a coal-dust motor, but the results were not encouraging enough to try it in a motor vehicle. Therefore, in the early 20's the I.G. Farben bought the rights to the Bergins patents and started developing coal hydrogenation. Because the development of the petroleum industry in the world, as we know it today, could hardly have been anticipated in 1925, the I.G. Farben, supported by a prognosis of geologists of the American federal oil conservation board that the oil reserves of the world would be depleted in about 7 years, convinced the German government that, if Germany wanted to become independent of oil imports, she would have to resort to the more expensive conversion of coal to liquid fuels, whereby simultaneously more jobs for Germans could be created. On this basis the I.G. Farben negotiated successfully some tax concessions and higher duties for oil imports. Then in 1926, i.e. only about three years after the initial experiments, the Leuna plant was built as a commercial-scale experiment and demonstration plant. In 1928 it operated at full capacity with antiquated equipment approximately as used in the NH_3 and methanol synthesis, i.e., reaction vessels of only 0.6 m I.D. and at a pressure of only 230 kg/cm^2. From the experience gathered in Leuna and further research in Ludwigshafen, the designs of hydrogenation plants with improved economics and equipment were developed and more than a dozen plants with individual capacities of up to 1 million metric tons* per year of gasoline were built from 1936 to 1943. Also, process variations like the TTH-process for producing lubricants, the hydroforming and DHD processes for producing aromatics and the desulphurisation of coke-oven benzene, were perfected and applied on a commercial scale. New and larger equipment was developed in the steel mills. The heaviest piece--the hot catch-pot for 700 kg/cm^2 pressure--weighed more than 150 tons and was the maximum the railway could transport. The working pressure had to be increased from 230 kg/cm^2 in Leuna for lignite coal, to 320 kg/cm^2 for bituminous coal with chlorine as catalyst and to 725 kg/cm^2 for bituminous coal with iron as catalyst, in order to improve yields and product qualities. Research in Ludwigshafen and commercial results in Welheim proved that extraction of coal before hydrogenation was uneconomical, due to difficulties in the filtration. Therefore the only extraction plant was converted to bituminous coal tar. Since this plant had only four small stalls, it forced the replacement of the 300-at.** saturation step by direct hydrocracking at 700 at.

The planning of the hydrogenation plants was directed towards an improvement of their economics by combining them with plants for the manufacture of rubber and chemicals. The hydrocarbon off-gases were cracked in electric-arc furnaces, or by partial combustion with oxygen, to acetylene and the hydrogen liberated by these processes was returned to the hydrogenation plants. Since the hydrogen accounts for about half of the manufacturing costs of gasoline from coal, significant savings were realized and the capacities of those plants, which were invariably determined by the hydrogen supply, were sharply increased.

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* 'Tons' in the following text refers to metric tons.

** In this text, 'at.' refers to the technical atmosphere, 1 kg/cm^2.

2. The Chemistry of Coal Hydrogenation and the Advantages and Disadvantages of Some Operating Schemes

The chemistry of coal and oil hydrogenation is very complex; some facts, however, are known. When the mixture of finely ground coal is heated in high-boiling oil fractions, the large coal micelles disintegrate at about 260°C into smaller molecules. The increase in surface area of the coal particles absorbs more "paste" oil and the coal paste becomes stiff-flowing from about 280°C, until at about 380°C the hydrogenation has proceeded far enough to convert much of the coal to asphalts. Figure 3(6) shows this viscosity-temperature dependence of coal paste containing 52% solids. This phenomenon limits the possibility of preheating the coal paste by heat exchange.

When the coal paste leaves the preheating system at 420 to 430°C and enters the reaction vessels, about 90% of the coal is converted to benzene-soluble compounds. In the reaction vessels the temperature rises autothermally from about 425°C up to 480°C to 490°C, at which point it is then held by the addition of 'quench gas' (hydrogen). The heat of reaction developed depends on the reaction temperature, on the type and origin of the coal, on the catalyst system used, and on the hydrogen partial pressure. To amplify these remarks consider the hydrogenation of bituminous coal at 700 kg/cm^2. At lower reaction temperatures, the heat of reaction is lower and rises from about 350 kcal/kg at 450°C somewhat exponentially with temperature up to about 530 kcal/kg at 490°C reaction temperature and 700 at. pressure. It is this exponential increase of the heat of reaction, and therefore quench gas consumption, that can cause temperature runaways. Lignite coal develops more heat of reaction than bituminous coal and, in turn, bituminous coal produces about twice as much as vacuum residue or bitumen. The better the catalyst the more completely are the products hydrogenated and the higher is the reaction heat. For coal the hydrogenation reaction is clearly noticeable from about 280°C upward. But the cracking of the large molecules derived from coal, into products in the boiling range below 360°C, requires a reaction temperature of at least 430°C. The hydrogen

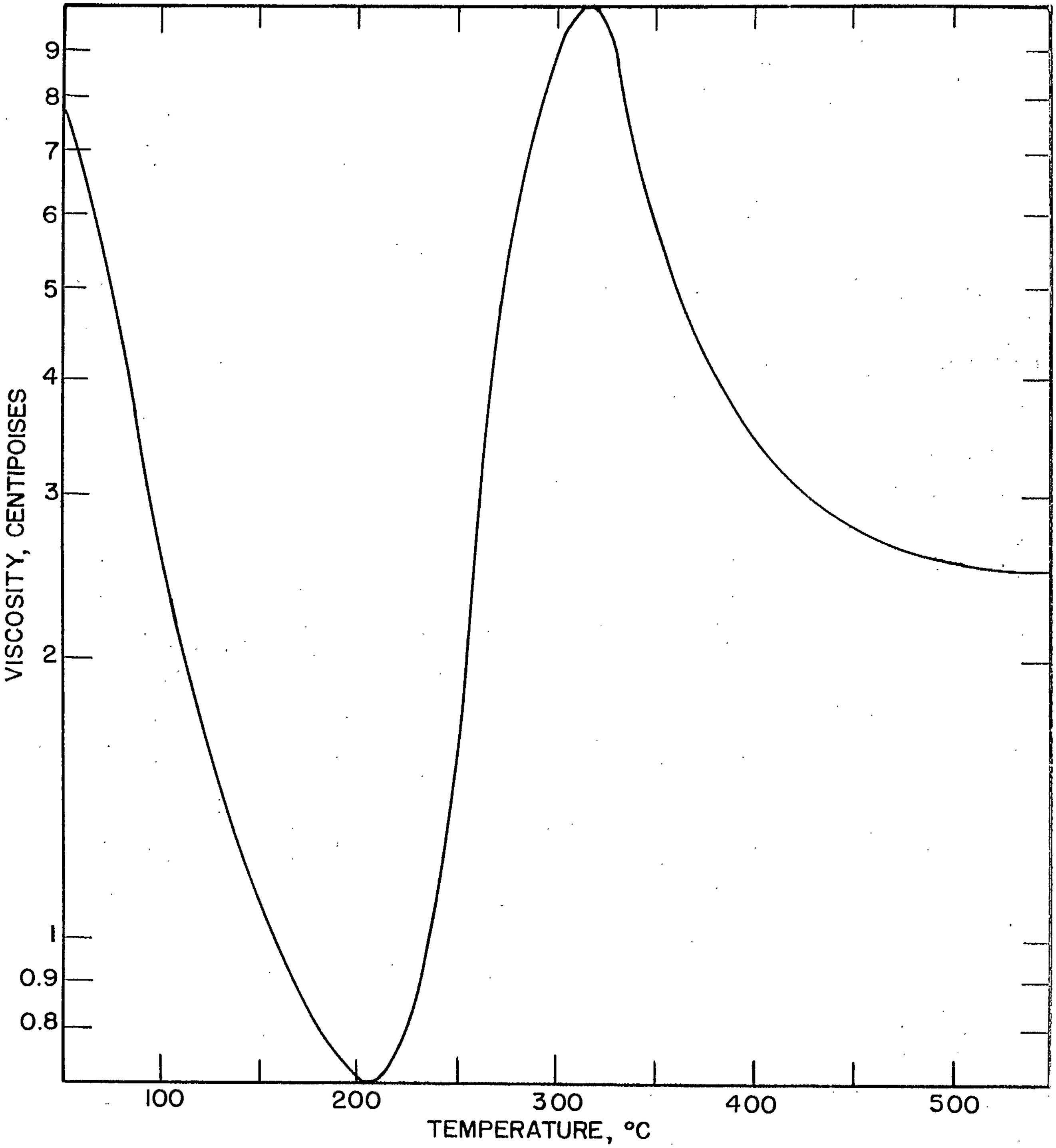

Figure 3. Viscosity of coal paste with 52% solids versus temperature.(7)

reacts only to a negligible extent with the coal in the paste directly. Most of the hydrogen is transferred via hydrogenation of the oil surrounding the coal particles, which act initially as catalyst support. A good example of this type of hydrogen transfer is the extraction of coal in which tetraline with 10% cresole is used as hydrogen carrier. Under these conditions about 70% or more, depending on the extraction temperature, of the coal is converted to "extract", an asphaltic substance with a melting point of 100 to 220°C. Tetraline can be replaced by middle oil fractions plus hydrogen with the same result, as, for instance, in the Uhde-Pfirrman, I.G. Farben, and Union Carbide and Carbon processes. A variant of this is the Varga process. Extracting the coal before hydrogenation, however, involves one or more additional steps and is in small plants more expensive.

In the liquid phase, coal hydrogenation must be operated so that the quantity of oil, boiling higher than 325°C to 360°C, obtained from the distillation of the product from the cold receiver plus the oils from the processing of the hot catch-pot discharge, is at least sufficient to replace the oil used in pasting the coal, charged to the system. This is done by balancing reaction temperatures against throughput. The operation can also be conducted so as to produce an excess of heavy oil. By this method the percentage yield of liquid products is increased, while the required reaction volume, the hydrogen consumption and the hydrocarbon gas formation are significantly reduced.

Figures 4 to 6 show flow schemes of three different modes of operations, which will be discussed in the following paragraph(7)(8). All quantities are given in metric tons per ton of final product.

Figure 4 shows the operating schemes of a standard 700-at., liquid-phase coal hydrogenation, combined with the standard 300-at., two-stage vapour-phase treatment of the liquid-phase products to produce gasoline only. For one ton of gasoline 1.844 tons of hydrogenation coal is required and the centrifuges have to process 2.277 tons to produce 1.912 tons of paste oil, sufficient to give a coal paste with 52% solids. This is too viscous to be heated in heat exchangers above 270°C. Consequently, for these

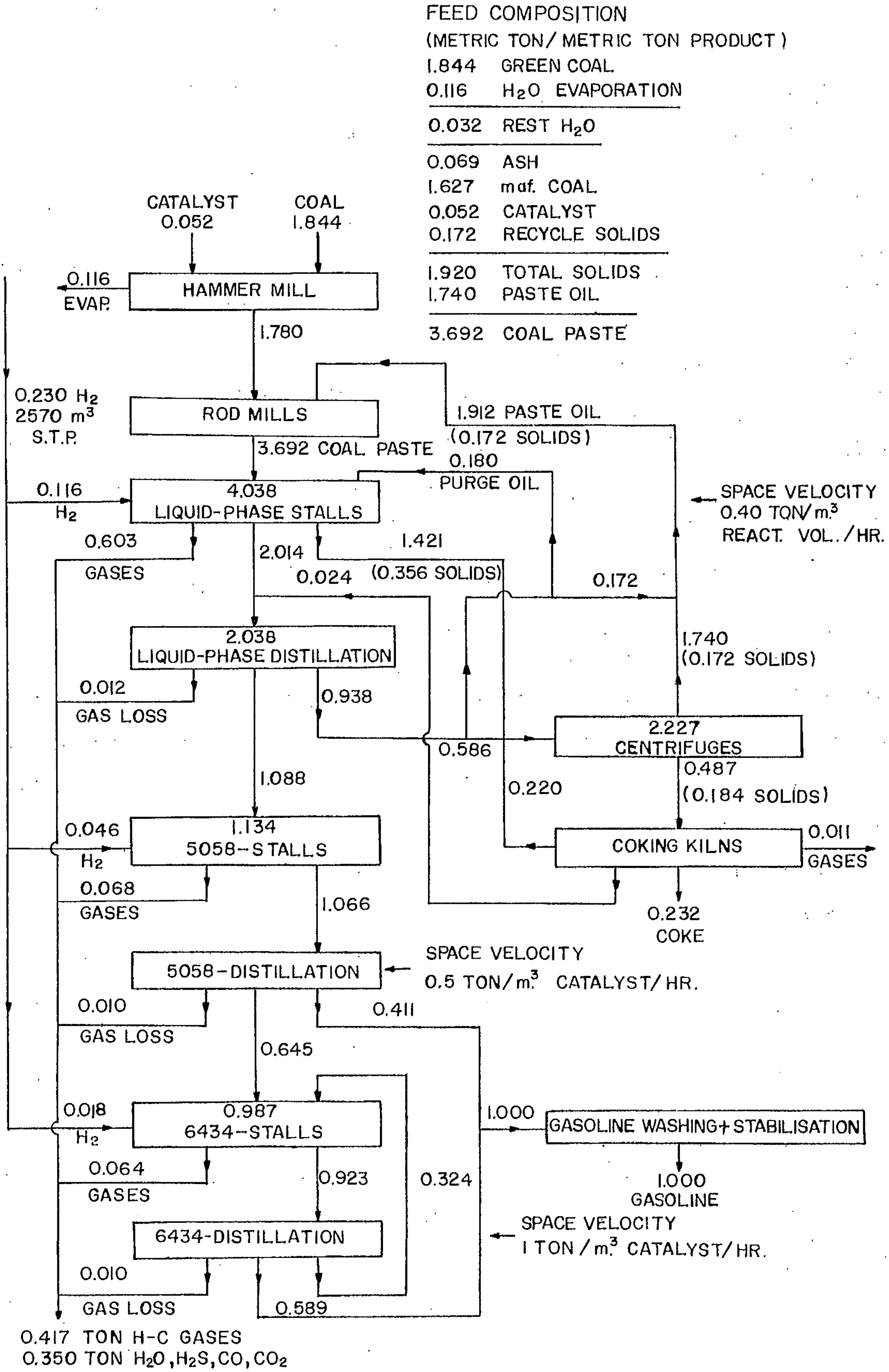

Figure 4. Flow scheme of hydrogenation of low-ash bituminous coal to motor fuel. (Tons per ton of product)

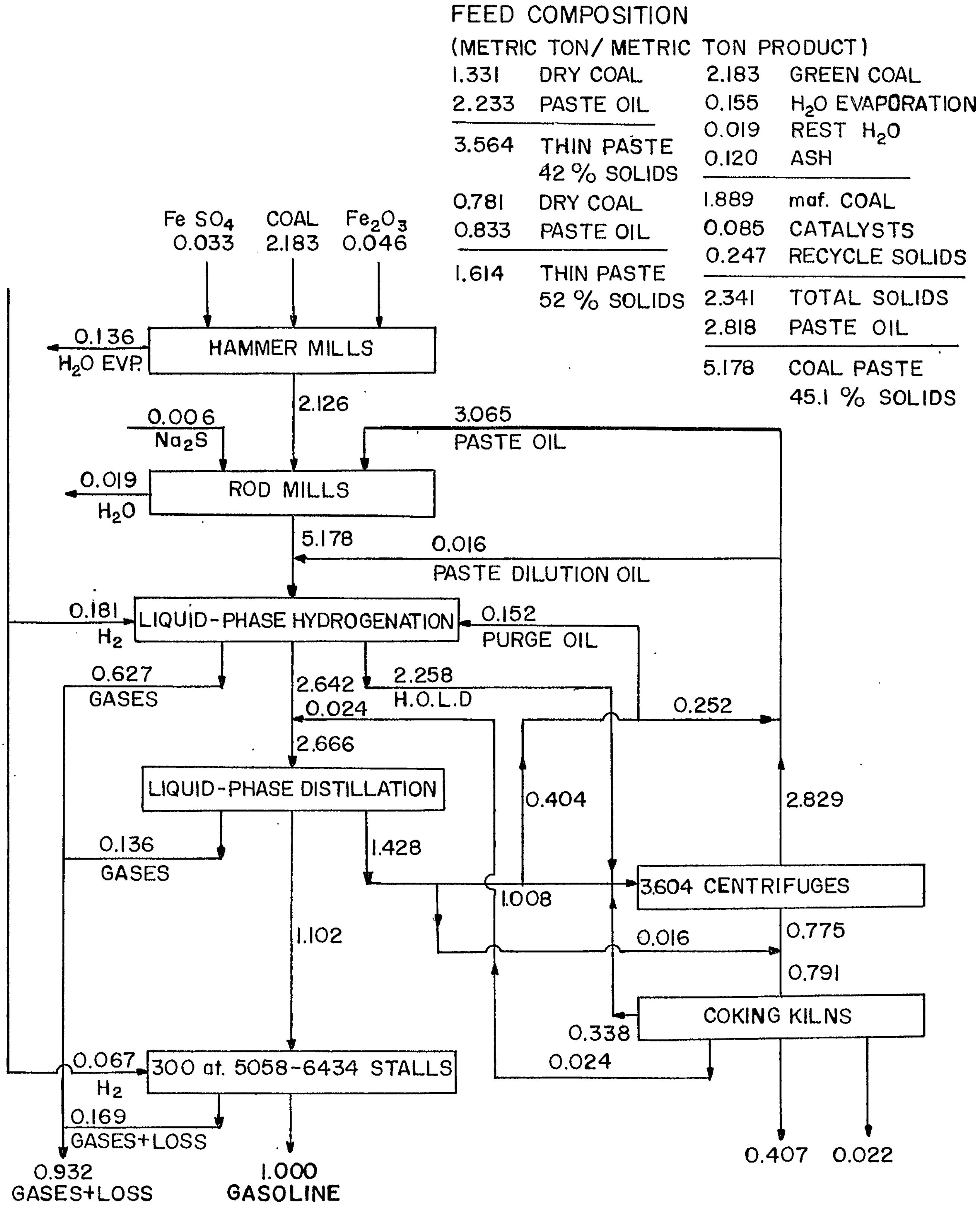

Figure 5. Flow scheme of hydrogenation of medium-ash bituminous coal to aviation fuel, incorporating partial preheating of the coal paste by heat exchange. (Tons per ton of product)

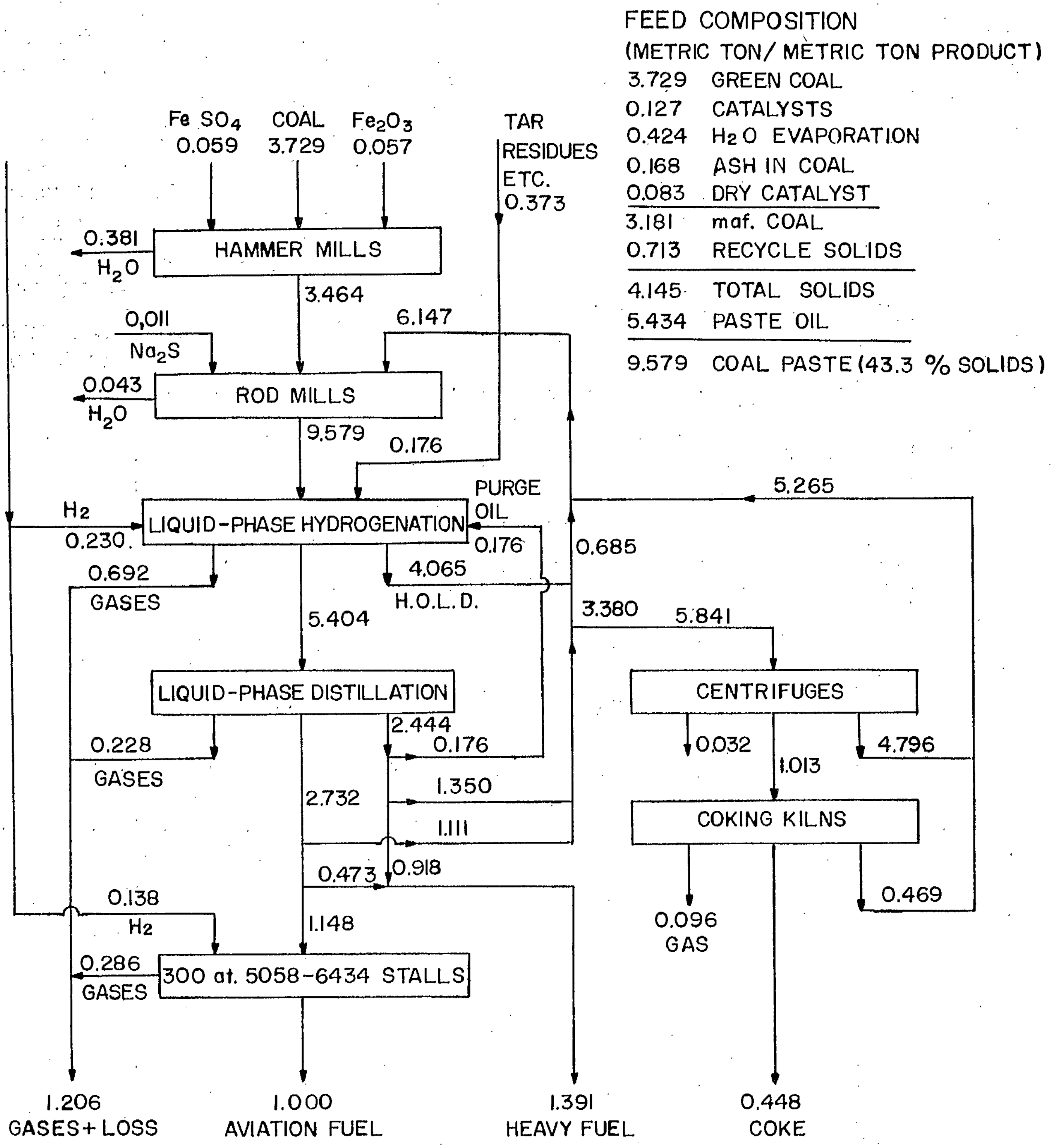

Figure 6. Flow scheme of hydrogenation of medium-ash bituminous coal to aviation fuel and excess heavy fuel oil, incorporating partial preheating of the coal paste by heat exchange. (Tons per ton of product)

700-at. systems, a large gas preheater with up to 30 vertical U-tubes (of 110-mm I.D. and 16-m length) is required. Per ton of product, 0.229 ton of hydrogen is used and 0.767 ton of hydrocarbon gases is produced, containing about 0.101 ton of hydrogen, i.e. about 44% of the total hydrogen consumed. Reaction volumes of 4.1 m^3 at 700 at., and 2.22 m^3 at 300 at., are required. To preheat the 3.692 tons of coal paste from 130°C to 430°C requires 581 Gcal*, and to preheat 3.7 m^3 recycle gas from 50° to 430°C requires 454 Gcal; the total for both is 1,035 Gcal, of which about 123 Gcal, or 11.9%, are supplied by injecting coal paste into the bottom part of the second converter; 365 Gcal, i.e. 35.3%, are supplied by heat exchange with the overhead products and gas from the hot catch-pot; and about 547 Gcal, or 52.9%, are inserted in the gas-fired preheater. Later, all the coal paste was preheated together with the entire recirculation gas in the heat exchanger, thus reducing the load on the preheater to about 524 Gcal with simultaneous improvement of the quality of the reaction products.

Figure 5 shows the operating scheme of a plant built one and a half years later. In this plant, about 65 to 70% of the coal paste was diluted to a concentration of 41 to 42% total solids so that it could be preheated with 85% of the recycle gas in a series of three heat exchangers up to 430°C. It was then mixed with the thick coal paste containing up to 55% solids and the remainder of the recycle gas, preheated up to 280°C. Mixing these two streams resulted in a temperature of about 375°C, at which the viscosity of the mixture was low enough to be further heated in another section of the preheater with satisfactory heat transfer rates, temperature and pressure differences. Preheating the feed and recycle gas for one ton of product required, however, 1,270 Gcal, of which about 70% were supplied by heat exchange and 30%, or 368 Gcal, in the preheater, i.e., a saving of about 30% preheater capacity, or 156 Gcal, corresponding to about 0.9 wt % of the hydrogenation coal used.

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* Gcal = 10^9 cal.

The savings in capital costs for the somewhat smaller preheater are diminished by the two additional heat exchangers required. The eventual savings are further reduced by the necessity to process 2,258 tons HOLD* instead of 1,421 tons, and to distill 2,642 tons instead of 2,038 tons; these differences are only partly due to the differences in the coal treated. The volume of coal paste to be injected increases to 5.178 tons, compared with 3.692 tons, i.e. 40% more. This shortened retention time, and the enormous recycle of heavy oil which had been subjected to high temperatures in the previous passes, explain in part the less favourable chemical results of this mode of operation: 8.5% more hydrogen consumption, stipulated by 25% more total hydrocarbon gas formation, not only in the liquid phase but also in the vapour phase, and therefore 16% higher consumption of hydrogenation coal. The reaction volume required increased correspondingly by about 49% to 6.1 m^3 in the 700-at. liquid phase, and by 2.5% to 2.39 m^3 in the 300-at. vapour phase.

These shortcomings were improved in a later plant, the flow scheme of which is shown in Figure 6. Although heat exchange of 2/3 of the coal paste as thin paste is incorporated as with the previous flow scheme (Figure 5), a greater throughput has been achieved by diluting the paste oil with high-boiling middle oil, which decreases the viscosity of the paste oil and increases its heat transfer. This middle oil portion evaporated in the preheater, and necessitated a HOLD recycle. Heavy let-down recycle, however, does reduce the over-all retention time of the heavy conversion products of the coal paste. Therefore, the throughput could be significantly increased to 0.600 ton of maf** coal per m^3 reaction volume compared to 0.309 ton per m^3 in the second flow scheme and 0.396 ton in the standard flow scheme. This increased throughput made possible a production of excess heavy oil, which when mixed with a portion of the middle oil was sold as marine fuel oil. The shorter retention time resulted in less cracking and was associated with less hydrocarbon gas formation (50.4% against 93.27) and less hydrogen consumption

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* HOLD = Heavy oil let down.

** maf = moisture and ash free.

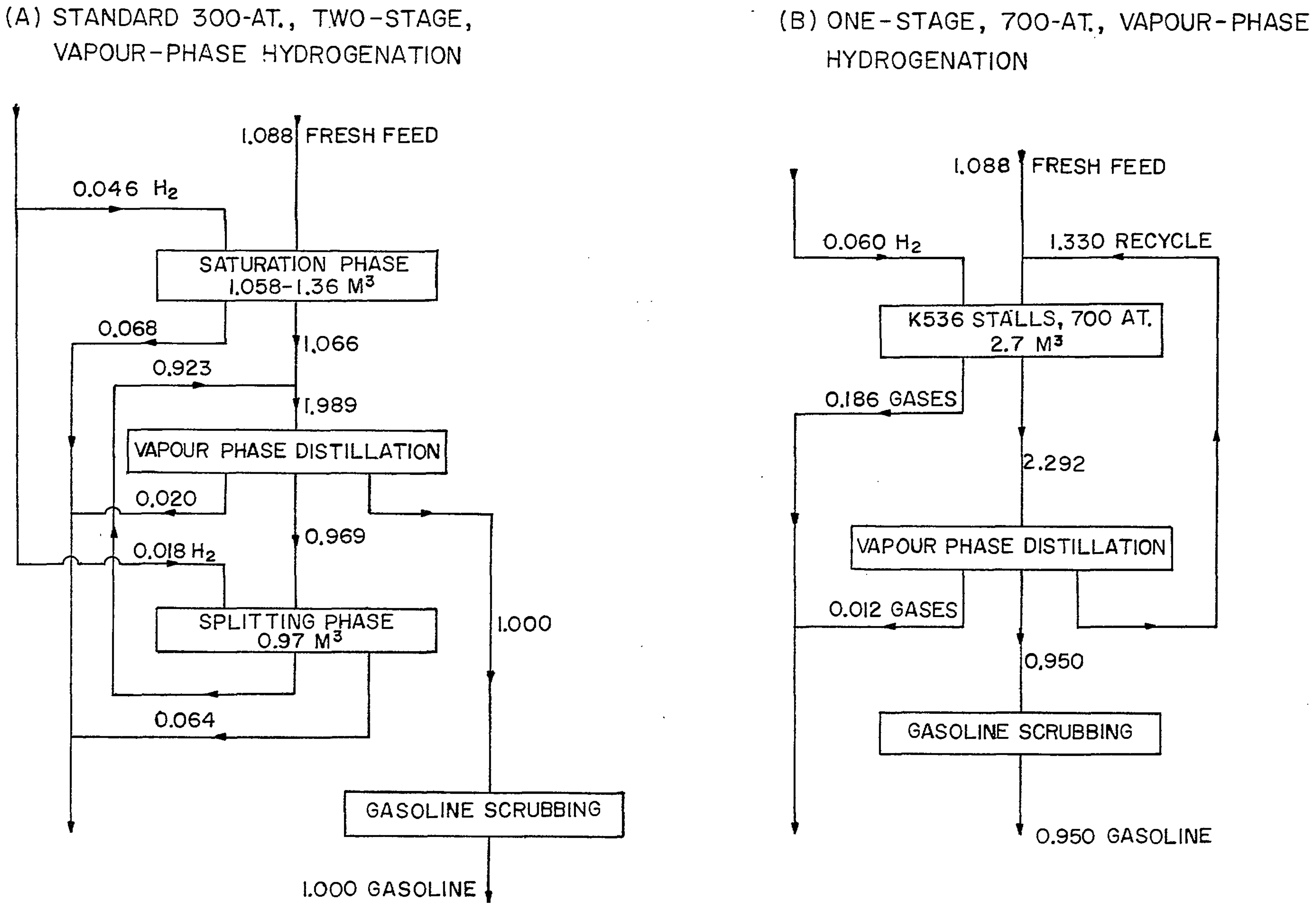
(15.4% against 24.8%). This mode of operation is particularly suitable if extraction of tar acids is contemplated. The shorter retention time in the liquid-phase vessels leads, however, to a less refined product, which in the vapour-phase treatment requires more hydrogen and yields more hydrocarbon gases. While in the standard process 1 ton of aviation gasoline requires 1.088 tons of middle oil plus gasoline from the liquid-phase operation, flow scheme 3 requires 1.148 tons, i.e. 5.4% more. The load in the residue-treatment plant seems to be high, 100.7% of the dry coal fed to the process as compared with 111.4% in flow scheme 2 and 82.3% in the standard flow scheme, but per ton of total product it is only 10% higher, due to the higher ash content of the coal, than in the standard process. If the throughput and the dilution with middle oil would be further increased, the process would change over into the "Uhde-Pfirrman" process for the extraction of coal, resulting in a still heavier product, namely extract. The HOLD, however, must then be filtered.

The products obtained from the liquid-phase operations have to be further treated in the vapour-phase operations. Those products boiling below 350 to 360°C from the 700-at. and below 325 to 335°C from the 300-at. liquid phase are passed, together with about 1.5 to 2.0 m^3 hydrogen recycle gas per ton of feed oil, in order to maintain a sufficient hydrogen partial pressure at the end of the reaction space over fixed-bed catalyst, either in two stages at 300 at. or in one step at 700 at. With the 300-at. process the first stage with a concentrated tungsten disulphide catalyst serves as a so-called saturation step to eliminate heterocyclics containing oxygen, nitrogen and sulphur and to saturate double bonds with no appreciable cracking at lower operating temperatures of 390 to 420°C. The second step serves to lower the molecular weight of the refined middle oil to the boiling range of gasoline at about 60% conversion per pass. A diluted catalyst, usually 10% tungsten on alumina, was used and since the temperatures had to be somewhat higher, 420 to 450°C, the desired degree of splitting and isomerisation could be obtained, and the required octane rating and vapour pressure of the gasoline were achieved by selecting the cut temperatures in the distillation and stabilization. The non-converted middle oil was recycled to extinction.

The running time of a 5058 saturation system was up to 3 years, of a 6434 splitting system only about 1 1/2 years, and a K536 system less than one year. This period is governed by catalyst activity and by feed material to be treated. The more asphaltenes or oxygen-containing compounds and trace metals there are in the feed, the higher is the carbon deposition on the catalyst and the lower its activity. The higher the operating temperatures, the higher the gas formation and hydrogen consumption and the shorter the catalyst life. During the operation period of a vapour-phase system the operating temperatures have to be raised steadily until the yield becomes too low to be economical. The 5058 systems were completely self-sustaining in terms of heat and had electrically heated preheater U tubes, while the cracking systems had gas-fired preheaters with 12 to 16 U tubes.

There is a distinct difference between the reaction of a liquid-phase system and that of a vapour-phase system. In the liquid phase the catalyst consists of fine particles suspended in the asphaltic oil that remains liquid at reaction conditions. It has a higher activity per unit weight than the vapour-phase catalyst pellets of 1-cm diameter and 1-cm length. But in one vapour-phase vessel there were about 17.2 tons 5058 or 5.8 tons 6434 catalyst, while one liquid-phase vessel contained only about 0.61 ton of catalyst diluted by about triple this quantity of ash from the coal. The vapour-phase converters contained about 9 to 28 times as much catalyst. This is the reason why, in connection with less severity and a lower molecular weight of the charge, less hydrocarbon gas formation and less hydrogen consumption were achieved in the vapour-phase operation. In the liquid phase the specific gravity of coal was reduced from about 1.35 kg/1 to about 0.935 kg/1 of the product, i.e. 0.400 kg/1, whereas in the vapour phase the reduction of specific gravity was from 0.935 kg/1 to 0.805 kg/1, i.e. only 0.130 kg/1.

The flow schemes of a standard 300-at., two-stage vapour phase and a 700-at., one-stage vapour phase are compared in Figure 7(9). It can be seen that the one-stage treatment requires somewhat less hydrogen



(A) STANDARD 300-AT., TWO-STAGE, VAPOUR-PHASE HYDROGENATION

(B) ONE-STAGE, 700-AT., VAPOUR-PHASE HYDROGENATION

Figure 7 - Comparison of the flow schemes of a two-stage, 300-at., vapour-phase and a one-stage, 700-at., vapour-phase hydrogenation of the products from the liquid phase to motor fuels. (Tons per ton of fuel)

but generates much more hydrocarbon gases, due to the higher operating temperature of 490°C, as compared to about 435°C with the 6434 catalyst. The gasoline has, however, a significantly higher anti-knock value and is obtained in a lesser yield.

It has also been considered to replace the vapour phase by a catalytic cracker. But since, for the lignification of coal, hydrogen generating and compressing facilities are needed in any case, the costs of 25% increase in capacity of the hydrogen-manufacturing facilities are compensated by the higher yield of about 91 wt% against about 80 wt% of a catalytic cracker.

3. Economics of Coal Hydrogenation

In spite of a lower yield of sometimes less than 80 wt%, refining of 36°-API[*] crude by hydrogenation is at present out of the question, since the processing cost per barrel in standard refining practice is only about $0.42/bbl if hydrodesulphurization is not counted. But high-sulphur 7°-API[*] vacuum bottoms, costing about $1.97/bbl instead of $2.89/bbl, can be hydrogenated in the so-called Combi process to gasoline and diesel fuel, yielding 90.5 wt% of products at processing costs of about $1.30/bbl for a 80,000-bbl/day plant, i.e. comparable to conventional refining methods. Hydrogenation of coal, however, yields only about 55 to 65 wt% of saleable products in the boiling range of gasoline.

The costs of coal hydrogenation are more difficult to estimate. The German plants were very small, 5,000 to 8,000 bbl/day, compared with today's "standards" of from 40,000 up to 250,000 bbl/day for an average modern refinery. Therefore, the costs given in a 1952 estimate of the U.S. Bureau of Mines for a 30,000 bbl/day plant should be corrected correspondingly. This estimate, as well as those of the firms Ebasco and Bechtel, showed that in a 1,000,000-metric-ton-per-year plant, comparable to the late German plants with the exception of replacing the forged vessels by multi-shell vessels, coal can be hydrogenated to gasoline and light fuel oils at a processing cost of $4.71/bbl, so that the manufacturing costs of gasoline

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[*] °API = degree specific gravity of the American Petroleum Institute.

were about \$8.02/bbl or 19.1¢/gal. Included in this price estimate for gasoline were credits for about \$219,265,000 for 265,000 tons per year of chemicals produced besides liquid fuels(10). This estimation showed that the gasoline from coal in a conventional plant was about 1.5 times as expensive as that from crude. From the experience in Germany from 1936 to 1945, it would appear that the combination of 1/4 petroleum residues or coal tar pitch with 3/4 coal as feed, and integrating such a plant into a grid with chemical plants like methanol, ethylene, butadiene and other chemicals, offers a somewhat better over-all economy.

Table 3 shows a comparison of costs of liquid fuels from coal or residuum by hydrogenation per one ton of final product(11). The first column is an estimate of Ludwigshafen from about 1942 and is based on the average operating results of existent bituminous coal plants. The second column gives the figures of the Leuna works. Since this plant operated undisturbed for about 15 years, it can be assumed that the figures are reliable, actual cost figures. In spite of antiquated equipment, approximately as used for the ammonia and methanol synthesis and consisting of a large number of small units, the capital charges are only 8.3% of the total manufacturing costs compared to an estimated 15.1% for Ludwigshafen. The 15.9% capital costs, estimated in 1952 by the U.S. Bureau of Mines, contain the investment for the hydrogen plant and are therefore comparable to the Leuna figures which do not include the cost for the hydrogen plant. The capital costs still are \$1.91/bbl and therefore look prohibitive when compared with the investment costs for standard refineries. They refer, however, to a 30,000 bbl/day plant. It is possible today, by means of multi-layer vessels with much larger reaction volume, to reduce the investment considerably. Since all the high-pressure vessels of one system contributed only about 20% to the costs of a complete system, increasing the size of the vessels and pumps to a multiple of the present value can therefore reduce the other 80% of the costs almost correspondingly(12). The expenses for starting materials are not too different for all coal plants compared here. The hydrogenation of oil, however, shows that higher raw-material costs are more than offset by lower operating costs.

TABLE 3

Comparison of Costs of Hydrogenating Coal to Liquid Fuels

	Ludswigshafen(9) (estimated 1938)		Leuna(8) (actual 1942)		U.S. Bureau(10) (estimated 1952)		Oil Combi(14) (actual 1958)	
	RM/ton Prod	%	RM/ton Prod	%	$/ton Prod	%	$/ton Prod	%
Coal	39.59	16.85	30.67	16.16	11.13	19.56	-	-
Catalysts	5.	2.13	6.23	3.28	2.89	5.06	1.73	6.87
Oil Feed	-	-	-	-	-	-	13.46	53.44
Hydrogen	126.	53.60	93.27	49.12	-	-	-	-
- Credits	71.20	30.35	54.63	28.79	-	-	0.56 for sulfur	
Fuel Gas	16.20	6.89	12.31	6.47	6.40	11.27	0.36	1.31
Electric Power	14.10	6.00	5.48	2.88	2.97	5.21	-	-
Steam	6.90	2.19	19.53	10.29	-	-	-	-
Water	1.90	0.81	2.04	1.07	0.05	0.09	0.05	0.19
Operating Labour	14.15	6.02	7.24	3.81	5.38	9.46	1.19	4.72
Maintenance + Indirect	13.80	5.87	6.24	3.28	7.10	12.50	0.99	3.16
Payroll Overhead	2.85	1.21	2.11	1.11	2.32	4.06	0.30	1.19
Process Materials	1.40	0.60	4.06	2.14	2.87	5.03	0.31	1.23
General Materials	6.90	2.18	11.10	5.83	3.68	6.48	0.49	1.96
Research + Gen. Exp.	11.05	4.70	16.86	8.87	0.90	1.58	1.33	5.29
Taxes + Insurance	7.85	3.34	6.60	3.48	2.17	3.81	1.41	5.59
Capital Charges	35.40	15.09	15.75	8.29	9.03	15.89	2.71	10.71
Shipping Costs	3.	1.28	5.14	2.71	1.05	1.81	1.05	4.71
Manufacturing Costs	234.70	100 %	190.00	100 %	57.94	100 %	25.37	100 %
					$7.48/bbl		$3.27/bbl	

As can also be seen from Table 3, the most promising area for attempts to save costs is the production and compression of hydrogen, which account for about half of the total cost of coal hydrogenation. Another field for possible savings is in the coal required to provide heat and energy, which exceeds by one-fifth the quantity of oil fed to the hydrogenation proper.

The hydrogen, manufactured by steam reforming or electric-arc cracking of the hydrogenation off-gases, was about 15% cheaper than that manufactured from water gas. In 1943 the costs in Germany were about Mk 15 - Mk 24 per ton of bituminous coal and Mk 1.30 per man hour. The hydrogen consumption per ton of coal was about 53,700 SCF*, or 98,900 SCF per ton of product. At a cost of about Mk 1.27 per 1000 SCF, from cracked off-gas, this corresponded to Mk 126 per ton of gasoline. This may be compared with an estimate, made in 1940 for a German bituminous coal plant, of Mk 256 for gasoline made with hydrogen derived from coke. The actual costs were, however, only Mk 211, or 18% less, with H_2 supplied partly from a butadiene plant and partly from increased efficiency of the equipment.

This plant, which was designed for 350,000 tons per year, actually produced in 1943, with practically unchanged equipment, about 452,000 tons of aviation gasoline annually. This meant, in effect, that the capital charges per ton of product had been reduced by 22.6%. Since the capital charges of this plant were originally about 15% of the manufacturing costs, or Mk 35.40, the increase in capacity contributed Mk 8.00, or 3.4%, to the savings in manufacturing costs.

If, from the cost of one ton of gasoline (Mk 211), the cost of the hydrogen (Mk 109) and the 1.844 tons of coal (Mk 43.30) required to manufacture one ton of gasoline are deducted, there remains only Mk 58.70 allotted for all other expenses, including capital charges, i.e. only 27.8% of the cost of the gasoline product. This indicates that efforts to improve the economics should be directed more towards the chemistry of the process than to improvements on the equipment.

If hydrogen is made from CH_4 and C_2H_6 by oxygen combustion under pressure, with simultaneous production of ethylene or acteylene, the

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* SCF = Standard cubic foot (760-mm Hg and 0°C)

credits thus obtainable will lower the cost of hydrogen and its compression quite considerably.

Eventually, carbon monoxide conversion can be omitted if the CO content is only a few percent, as in the case of converting the hydrogenation off-gases to ethylene and supplying only 10% from water gas to start up the plant. Experiments in Ludwigshafen have shown that CO is converted in the liquid-phase operation to an appreciable extent to liquid products and is thus continually eliminated from the recycle gas. This procedure could save about 5.2% of the cost of the hydrogen, or about 2.6% of the cost of the product. If it is anticipated that the prices for oil and gas will increase in the future it may be profitable to sell the gas and manufacture the hydrogen from coal by pressure gasification; for instance, in Lurgi gas producers or in Koppers Totzek burners, or by gasifying the coal at full pressure thus saving the entire 40% of the compression costs. The experiments in Ludwigshafen showed that even with CO concentrations of up to 40% the asphalt concentration is only slightly increased. The compression costs to 700 at., for instance, were established in Germany to be Mk 0.425 to 0.635 per 1000 SCF, i.e., 44% of the total costs of compressed hydrogen, and compressing it to 25 at. amounts to more than half of these costs. Therefore, if hydrogen can be produced 15% cheaper than from water gas and if half of the compression costs can be eliminated, a total savings of 42.2% of the hydrogen costs, or 21.1% of the product costs, can be realized, meaning that gasoline can be produced from coal for 15.1¢ instead of 19.1¢ per gallon. This mode of hydrogen manufacture was partially incorporated in two of the later German plants (Bruex and Blechhammer).

The consumption of fuel gas, electric power and steam amounts to between 13 and 19% of the product costs and represents about 120% of the coal fed to the hydrogenation proper. The savings effected by preheating the coal paste in heat exchangers are only a small part of the above percentage and are offset by higher expenditures for heat exchangers and processing of the larger volume of heavy oil recycle. The easiest way to effect savings in heat is to build larger units with less surface area per unit volume and to reduce the number of steps connected with heating and cooling in the total process, which will be discussed in more detail later on. One example is the combination of the distillation for the saturation and splitting step into one distillation, which has been practised in Germany in some smaller plants. The use of the heat of reaction in the liquid phase to preheat a small part of the coal paste has been carried out successfully, but no attempt has been made to preheat all the coal paste and the recirculation gas or the vapour-phase feed by this method, which would save heat and investment costs by elimination of the heat exchanger entirely. The consumption of electric power has been reduced only insignificantly by using expansion machines in the oil scrubbing of the recirculated hydrogen. Almost 50% of the energy produced in the power plant was used up by the compression of the hydrogen to 325 at. Only at a very late stage in the development was hydrogen compressed to 20 at. by rotational compressors with direct turbine drive, thus reducing the investment for turbo generators and other electrical facilities very significantly.

Of the central German plants, only Leuna processed lignite coal at 230 at.; the other plants processed lignite coal tar at 325 at. Thus, the capital costs were considerably less with lignitic coal than for those plants processing bituminous coal in a 700-at. liquid-phase operation. By hydrogenating lignite coal tar, with molydenum on char as catalyst, the efficiencies of the individual units were more than doubled as compared with the standard coal hydrogenation plant, and substantial savings could be realized under special circumstances.

4. Improvements of the Coal Hydrogenation and New Processes

From the coal and oil hydrogenation processes, some variants or newer processes were developed in 1941 when the demand for higher octane gasoline rose(13). The DHD process, operating at 500 to 520°C and 30 to 50 at., and the hydroforming process, operating in Leuna at 10 to 15 at., were developed to produce gasolines with a high aromatic content. Variants and combinations of these processes are the catalytic reforming, the hydrodealkylation at 50 at., the hydrocracking at 200 at., the isomax and the unicracking processes, the H-oil process, and others.

It is well known that unsaturated or oxygen-containing compounds tend to polymerize when stored at lower temperatures. The processing of higher-molecular-weight feed in the vapour phase is, however, associated with higher carbon formation on the catalyst and necessitates higher temperatures, higher hydrocarbon gas formation, and higher hydrogen consumption. A process has been developed in which the overhead products from the liquid-phase hot catchpot, including product vapours and recycle gas, are passed directly over fixed-bed hydrogenating catalyst at 300 at.(14). The catalyst is an artificially precipitated support, containing promoters which give it greater activity than was attained with the 5058. This is necessary in order to convert the heavier asphaltenic oil vapours coming from the liquid phase and to resist being poisoned by the higher ammonia contents of the liquid-phase recirculation gas. The starting material for this so-called "Combi" process should not contain more than 1% nitrogen on moisture- and ash-free feed stock. Figure 8 shows the boiling curves and Table 4 shows some quantities of a product obtained by this process from a vacuum residue feed. It can be seen that the portion boiling above 350°C is reduced from 55 wt% to 25 wt% with only 2% hydrocarbon gas formation and 0.4 wt% hydrogen consumption. If this product is scrubbed with lye and water, it can be sold as fuel without further treatment in a vapour-phase unit. The higher fractions of the gasoline require, however, some reforming. A flow diagram of such a Combi system is shown in Figure 9. The manufacture of gasoline from vacuum residues by this method is, as the last column in Table 3 (page 22) shows, competitive with standard refining costs.

Experiments have shown that oil from coal hydrogenation boiling above 325°C can be successfully hydrogenated over 8376 catalyst in the vapour phase. Therefore it is not entirely excluded that this process could work at 700 at. for bituminous coal as well. By eliminating the separate vapour-phase operation, the plant costs as well as the operating costs could be reduced by roughly 23%; the hydrogen consumption would also be reduced by about 5%. The 27.8% capital and operating costs on the product would reduce then to 21.4% by 6.4%, and the hydrogen costs by 2.5%; together, a saving of

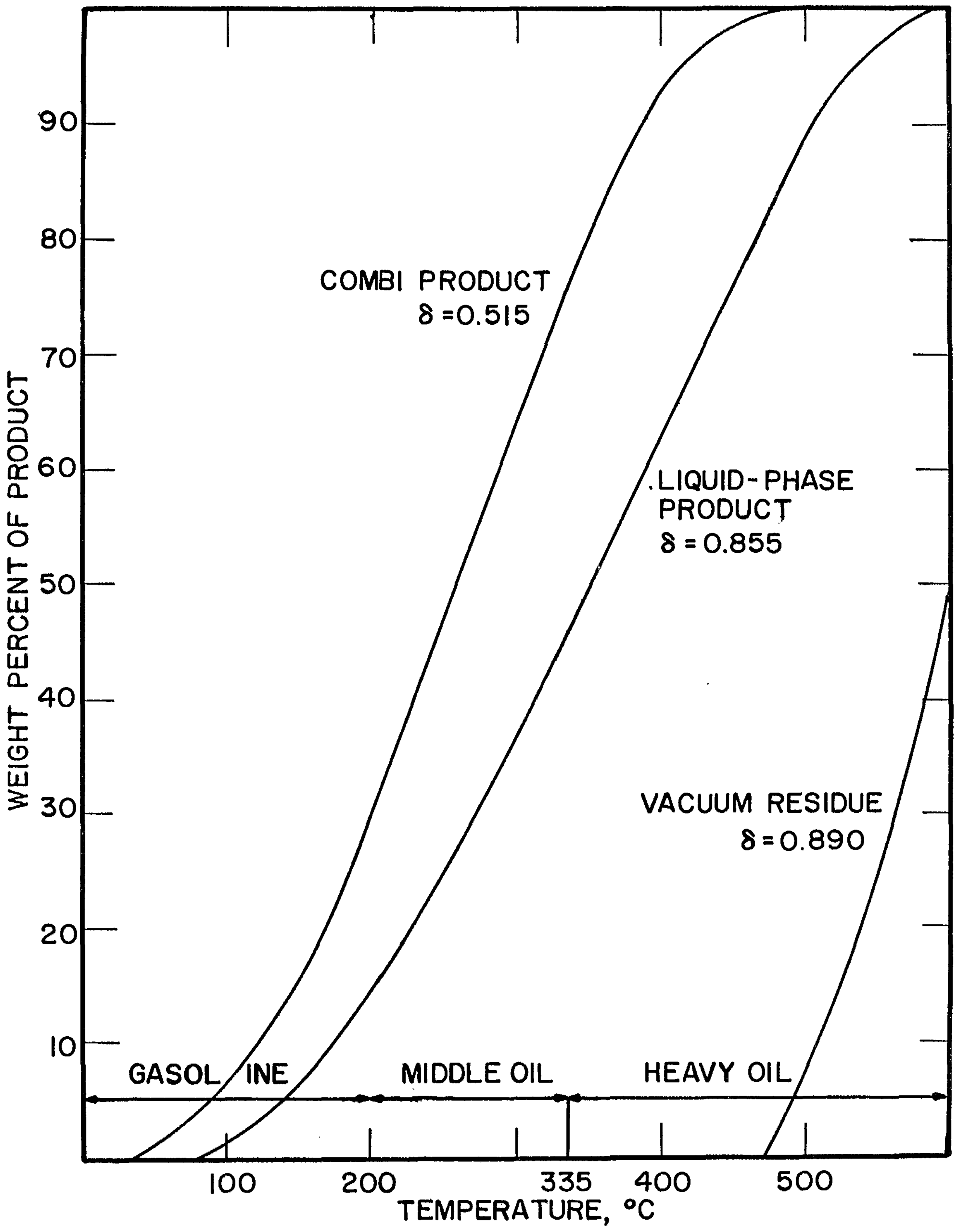

Figure 8. Boiling curves of products and feed-oil from liquid-phase hydrogenation and Combi hydrogenation. (14)

TABLE 4

Comparison of Characteristic Figures of Liquid-Phase and Combi Hydrogenation

		300-at. Liquid Phase	300-at. Combi System
H_2 requirements, m^3/ton feed		300	350
Yields, wt% of feed:			
$C_1 + C_2$ gases		4.6	5.6
$C_3 + C_4$ gases		2.6	3.6
H_2S		1.1	1.6
Liquid $> C_4$ products		90.0	87.5
Coke from hydrogenation residue		1.7	1.7
Sp. gr. of the hydrogenation product oil		0.855	0.815
Sulphur content of the hydrogenation oil, %		0.82	0.17
Gasoline:	wt%	14	30
Spec. grav. 15°C	kg/l	0.740	0.730
S content,	%	0.05	0.02
Boiling up to 100°C, Vol %		20	30
Gum test, mg/100g		>100	>5
Road octane number - clear		45	48
- leaded		56	60
Diesel fuel:	wt%	30	45
Spec. grav. 15°C	kg/l	0.840	0.840
S content,	%	0.80	0.45
B P A,	°C	6	12
Cetane No.		46	50
Heavy oil:	wt%	56	25
Spec. grav. at 50°C	kg/l	0.860	0.840
Conradson carbon,	wt%	0.15	0.04
S content,	%	1.0	0.3
mg NH_3/l		7500	100
End point, 760 mm Hg	°C	~ 600	~ 500

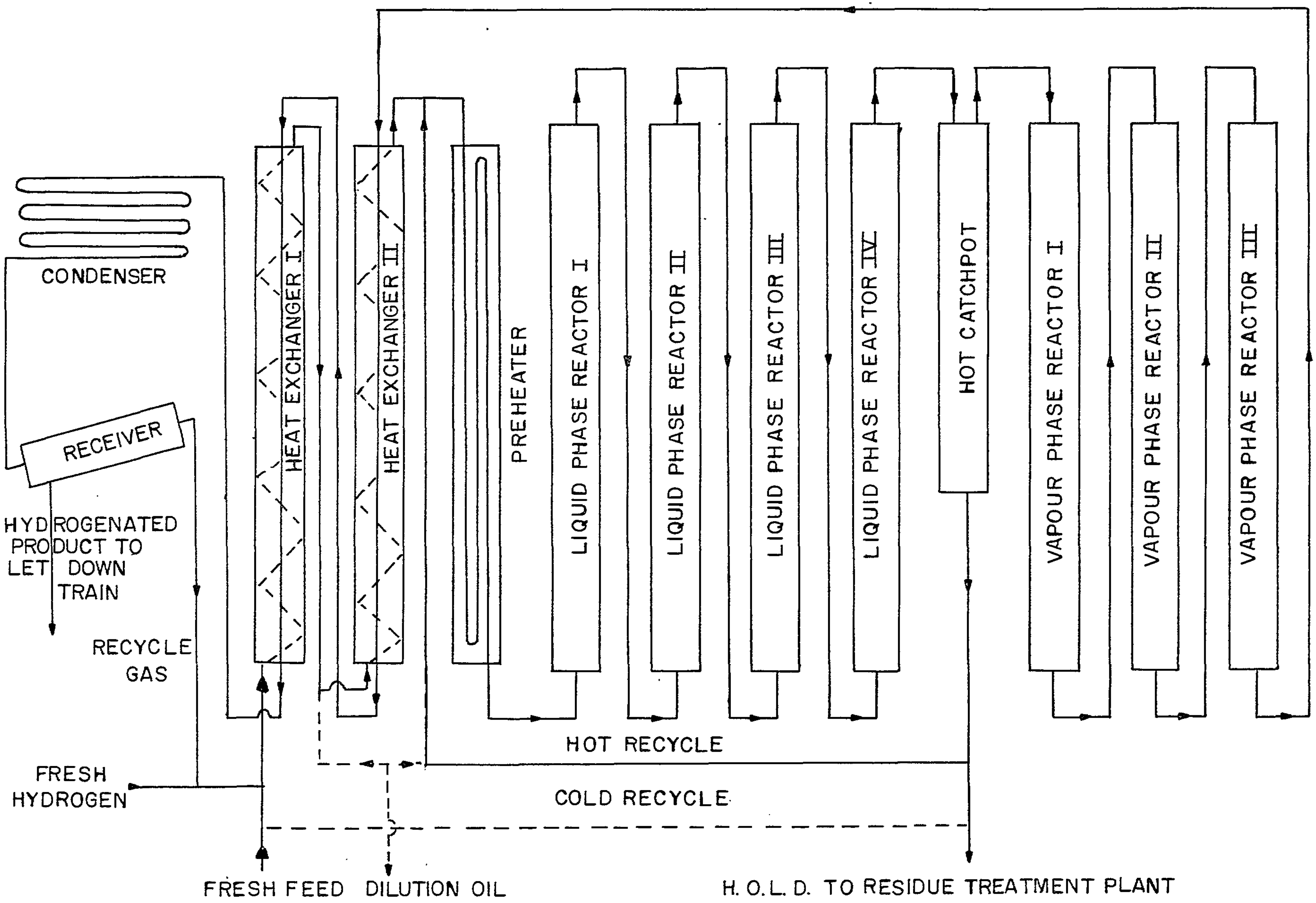

Figure 9. Flow diagram of the Combi hydrogenation.

8.9%. If the possible saving in hydrogen costs mentioned on page 24 are included, the total savings may reach 21.1 + 8.9 = 30.0%, thus reducing the cost of gasoline from 19.1¢/gal to 13.4¢/gal, which is almost comparable to today's average refining costs of 12.55¢/gal.

In the United States the so-called H-oil process has been developed in an attempt to improve on the liquid-phase hydrogenation. In this process, the fluid in the reaction vessels is recirculated inside the vessels at high speed, thus establishing a uniform temperature distribution and reducing the number of quench-gas inlets from 6 to 1. The licensee(22) of this process claims improved hydrogenation through using a larger amount of catalyst per vessel, by not impregnating or admixing catalyst to the feed but introducing the catalyst in form of very small pellets or granules to the vessel. The size and weight of the pellets are such that their settling velocity in the fluid equals its upstream velocity. Thus, essentially no catalyst is carried out of the vessel, and the solids concentration in the residue--and therefore the amount to be processed in the residue treatment plant--is much smaller. How far the increased catalyst volume, taking up more space than the impregnated catalyst, improves the hydrogenation of coal or other high molecular substances (since the molecules of the raw material are too big to enter the pores of the catalyst) is not yet established in a commercial operation. According to the Hydrocarbon Research Incorporated, the liquid product yields are 56 to 71 wt% and the cost of gasoline in 1963 could be 12¢/gal(22)

Further savings are possible by improving the chemistry of the process in other ways than by catalysts; for instance, by not recycling the unreactive solids and benzene-insolubles with the paste oil but eliminating them from the oil leaving the hot catch-pot. This can be done by processing the HOLD in a fluid coker, by solvent filtration, or by surface chemical methods which flocculate the undesirable compounds.

CHEMICALS FROM COAL BY HYDROGENATION

Contrary to the production of chemicals by oxidation of coal, hydrogenation yields valuable by-products, such as liquid fuel, in addition to such desirable chemicals as phenols, tar bases, and ammonium sulphate. The less severe the liquid-phase hydrogenation the higher is the percentage of oxygen, nitrogen and sulphur compounds left in the liquid-phase product and the more suitable it is for extracting the tar acids and bases. The less severe, however, the liquid phase treatment, the higher is the molecular weight of these compounds and the less desirable they are.

A large number of these compounds have been identified but many are still unknown. Table 5 gives the compilations of the names and approximate concentrations of these compounds in the liquid phase product.

During World War II, in Germany the recovery of chemicals from the coal hydrogenation products was neglected, since enough coal tar chemicals were available from the coke ovens, whereas liquid fuels were critical. Table 6 gives an incomplete compilation of the basic organic chemicals produced in the United States in 1967. It can be seen that the absolute amount produced was more than 41 million tons, or about 0.21 ton per capita per year. This table and Figure 10 show also that those compounds, with few exceptions, exhibited an annual growth rate since 1961 of double or more than the average of the chemical industry in the United States.

1. Chemicals by Extraction of Gas and Liquid Streams

1(a) Sulphur and ammonium sulphate

The recovery of sulphur and ammonia in the hydrogenation, as well as in the standard refinery processes, is mandatory. Most of the sulphur and nitrogen introduced into the processes from the feed materials, from the coke for hydrogen manufacture and from the catalysts is converted to H_2S and NH_3, which appear in the off-gases and waste water of the hydrogenation. From 20 to 40% of the sulphur in the coal is left in the coke from the residue-carbonization plant*. In the case of coal hydrogenation, only 60 to 80% of the total sulphur is recoverable. If oils and residues are processed, the sulphur recovery is 95 to 100% of the sulphur introduced.

The H_2S was usually recovered by scrubbing the gases with alcazid lye, an aqueous solution of sodium glycocoll (CH_2NH_2-COONa) containing 200 g/l calculated as Na_2CO_3 and a specific gravity of 1.17. The

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* Which converts the HOLD to coke and heavy distillate.

TABLE 5

Tar Acids and Bases in the Product of the Liquid-Phase Hydrogenation

Product		Weight % of total product
Tar acids:		
	Phenol	1.9
	O-Cresol	0.2
	m + p - Cresol	2.4
	Xylenols	1.6
	Total ----------	6.1
Aromatics:		
	Benzene	8.2
	Toluene	13.9
	Xylenes	15.4
	Ethylbenzene	2.8
	Napthalene	3.7
	Mixed aromatics	6.8
	Total ---------	50.8
Liquified petrol gas		16.4
Motor gasoline		15.6
Aviation gasoline		11.1
	Total ---------	26.7
	Grand Total ------------	100
	$(NH_4)_2SO_4$ --------------	11.25
	Sulphur --------------	0.72

TABLE 6

Production of Some Organic Chemicals and Intermediates in USA in 1967*

COMPOUND	Production, in 1000 tons/year	Growth rate, in % per year**	Price (ca) $ per ton	USES
Ammonia	12,000	14.9	$30.	Fertilizer
Urea	1,500	8.5	$80.	Fertilizer, plastics
BASIC ORGANIC CHEMICALS				
Ethylene	6,250	14.0	$60.	50% Plastics, 50% others
Acetylene	600	7.0		
Propylene	2,400	10.3	$150.	50% Plastics, 50% glycol
Benzene	3,700	10.8	$ 68.	Styrene, chemicals
Toluene	2,500	16.9	$ 62.50	Chemicals, explosives
Xylenes	1,650	10.0	$ 67.	Plastics, fibres
Cyclohexane	1,150	22.0	$ 64	Nylon, solvents
Phenol			$180.	
INTERMEDIATES				
Acrylonitrile	550	28.0	$300.	Fibres, rubber
Butadiene	1,550	8.3	$212.	Rubber, plastics
Cumene	450	20.6		Phenol, acetone
Ethylenedichloride	1,900	18.5	$180.	Vinylchloride, chemicals
Ethyleneoxide	1,200	10.0	$310.	Glycol, plastics
Formaldehyde	750	14.8	$187.	Plastics, chemicals
Propylenoxide	400	13.5	$300.	Glycol, chemicals
Styrene	1,800	12.7	$155.	Rubber, foam
Vinylchloride	1,500	19.3	$206.	Plastics, fibres
ELASTOMERS				
Butyl rubber	110	1.6		Rubber, plastics
Neoprene	150	2.4		Rubber, plastics
Nitrile rubber	75	8.9		Rubber
Polybutadiene) Polyisoprene)	385	40.5		Rubber tires
Styrene-butadiene	1,440	3.1		Rubber coatings, plastics
E-P-Terpolymer	40	89.0	$800	Rubber compounding
POLYMERS				
Phenolics	535	8.3		Hard plastics
Polyesters	240	16.5		Glass fibre reinforced plastics
Polyethylene:				
High density	525	24.2		Moulded plastic
Low density	1,520	14.8		Plastics, films
Polypropylene, no fibre	290	39.0		Moulded plastic
Polypropylene, fibre	1,300	15.0		Hard plastic
Polyvinyl chloride	1,250	14.3	$600	Plastics, fibres
FIBRES				
Acrylics	225	24.7		Fibres
Nylons	610	18.1		Fibres
Olefines	60	39.8		Fibres
Polyesters	300	37.3		Fibres

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* From American Petroleum Institute Yearbook, 1967.

** From Reference 18.

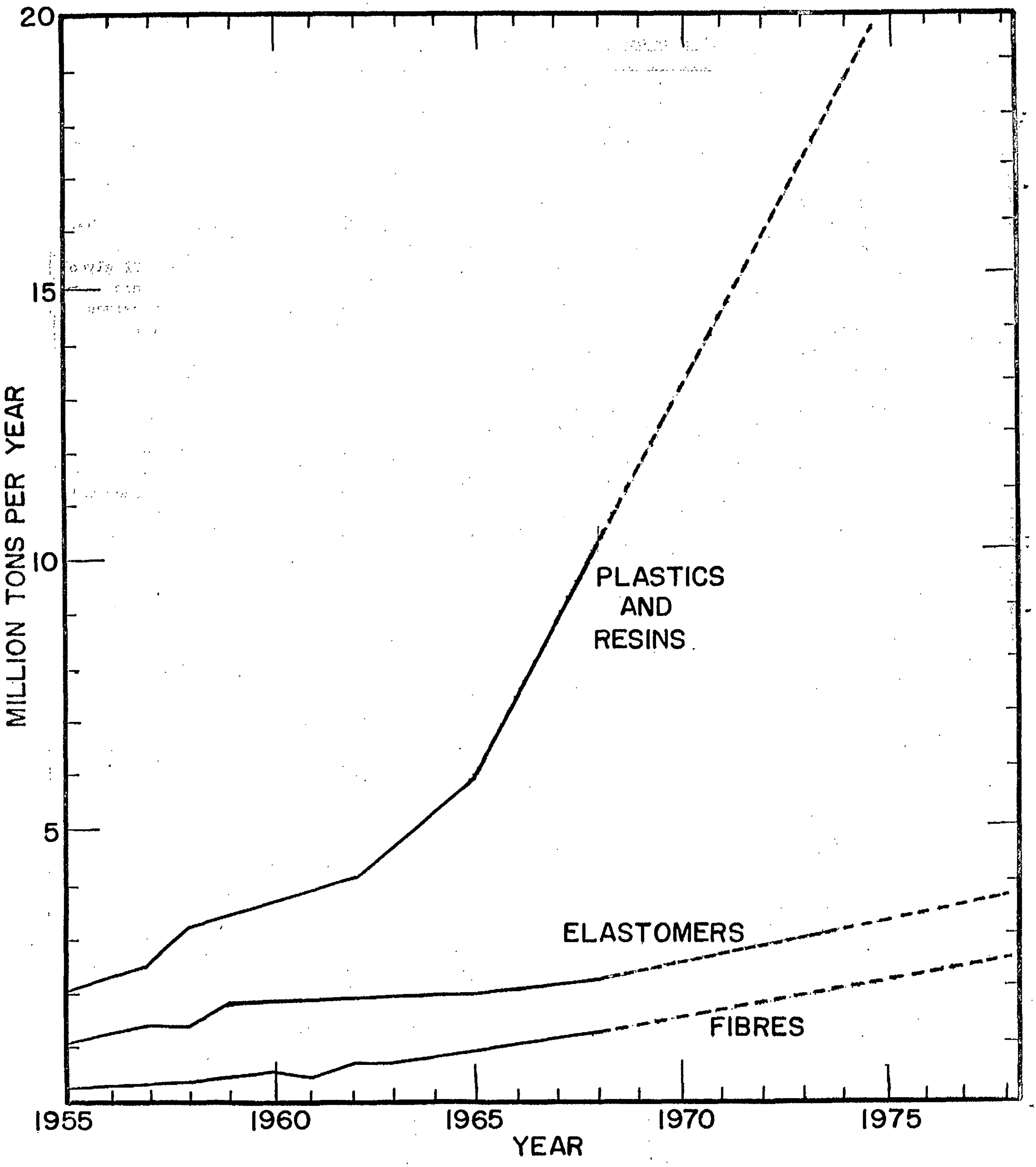

Figure 10. USA production of plastics, fibres and elastomers (from 1955).(18)

alcazid lye dissolved selectively the H_2S(15). The lye was regenerated with steam and the H_2S was burned in Claus ovens to elemental sulphur. The off-gases of the Claus ovens and part of the sulphur so obtained were burned to H_2SO_4 and used for the extraction and neutralization of the NH_3 from the gases and waste waters for the production of $(NH_4)_2SO_4$. The sulphur removal by active carbon was not as convenient as with alcazid lye, and all later plants used the alcazid process. This process did, however, remove the sulphur from the gases down to 1 to 2 mg/m^3, as compared with 100 mg/m^3 with the alcazid process. For the removal of CO_2 an aqueous solution of sodium alanine (CH_3CHNH_2-COONa) can be used. However, this compound dissolves both H_2S and CO_2 and can therefore be used only after the alcazid scrubbing. But in most later plants, CO_2 was separated in the Linde gas plant for the low-temperature separation of the ethane, propane and butanes from the "rich" hydrocarbon gas streams. From the converted water gas or methane reforming gas, the CO_2 was scrubbed by water at 20 to 25 at. pressure.

Most of the ammonia formed during the hydrogenation by breaking up the heterocyclic N compounds, and also to a small extent from the conversion of the nitrogen introduced into the system with the hydrogen, appears as ammonium sulphide in the waste liquors, from which it can be removed by aerating it with gas or nitrogen in a scrubbing tower at atmospheric pressure and boiling temperature. From the gas the H_2S is removed with alcazid lye, and the NH_3 is neutralized by passing the gas through H_2SO_4. The heat of neutralization evaporates enough water to precipitate from the saturated solution as much ammonium sulphate as is freshly formed.

1(b) Tar acids

As can be seen from Table 5 (p.32)(16), about 6% of valuable, low-boiling phenols are in the liquid-phase product along with 3.5 to 10 wt% high-boiling, oxygen-containing compounds. The worthwhileness of recovering these substances depends on their concentrations in the liquid to be extracted and on their market price. Good solvents for tar acids are liquid ammonia or aqueous 60% to 90% methanol, at low pressure; or, more cheaply, two parts of waste liquor (which already contains up to 6 g/1 phenol) to one part of oil at 75 to 250°C and 1 to 50 at. From the aqueous solutions, as well as from the product oils, the phenols can be separated by steam distillation, or, if waste liquor was used for the scrubbing of the oil, by extraction with low-boiling naphtha containing technical butyl-acetate. This solvent, named phenosolvan, extracts the phenols from the liquor down to about 100 mg/1. The other solvent used was technical tricresylphosphate, which extracts the phenols only to about 1.5 g/1 but, due to its high boiling point, makes the separation and purification of the individual phenols somewhat easier.

The dephenolized liquor, containing 100 mg/1, has in most cases to be further treated. It is diluted to about 10 to 20 mg/1 phenols, 200 g of sodium phosphate are added per m^3 of liquor and it is then fermented with bacterium diplococcus. The fermentation is carried out in open basins to 25 to 30°C and a pH value of less than 8, with good agitation. Air was introduced from porous plates at the bottom of the basin. The phenol content was reduced from 10 mg/1 to about 3 mg/1, and the dephenolized liquor could then be discharged into the river.

The Metasolvan process, as shown in Figure 11, operates at low pressure and extracts the tar acids from the product oil with 60 to 90% methanol in a countercurrently operated column. Entrained oil is scrubbed in a second column with light naphtha boiling at 70 to 110°C. In a third column column the naphtha is separated from the higher-boiling oil by distillation, and the oil-free methanol extract is dephenolized in a fourth column and the dilute methanol returns to the first column. 0.7 part of dilute methanol is sufficient to extract 1 part of product oil down to almost 0.36 g/1 tar acid content. The methanol content and the volume of the dilute solution determine the amount of phenols that can be extracted, but the higher the methanol content the more neutral oil is dissolved simultaneously.

The phenosolvan process extracts the tar acids from aqueous solutions. Since the phenosolvan, being an ester, dissolves to an appreciable extent in water, the countercurrent extraction was carried out in three horizontal contactors and the dephenolized liquor had to be steam-distilled

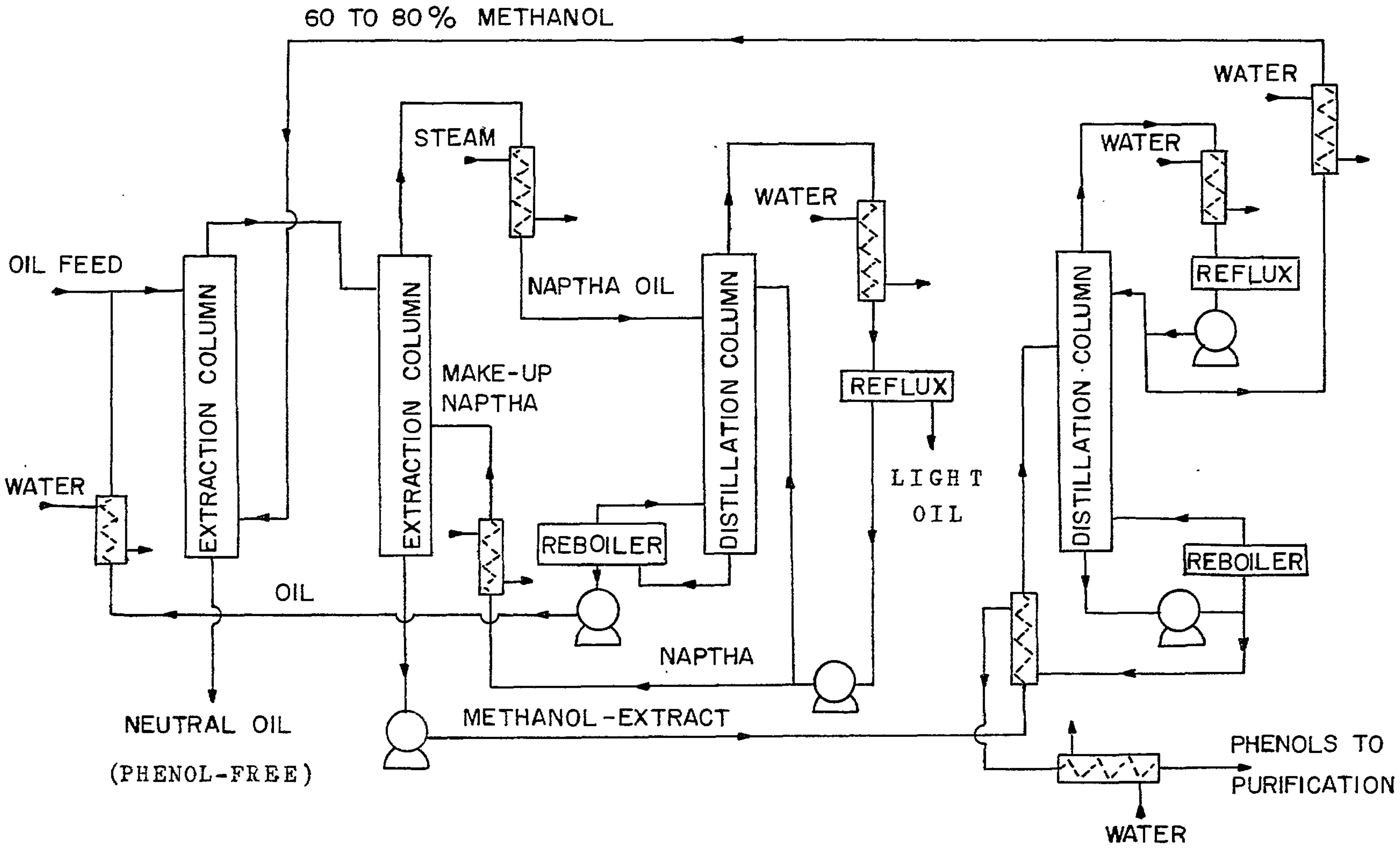

Figure 11. Phenol extraction from oil products.(11)

to recover the phenosolvan. The liquor left this column with a phenol content of about 100 mg/l. The phenosolvan extract was then separated from the phenosolvan in a second column, and after that in a third column at about 200 mm Hg vacuum at 150 to 170°C. About 0.1% phenosolvan remained in the phenols and was lost. A flow scheme of this process is shown in Figure 12.

1(c) Tar bases

Tar bases were extracted only on a pilot scale, because sufficient pyriding was available from the coke-oven operations. Tar bases can easily be extracted by scrubbing the gasoline-middle oil fractions from the liquid-phase product with diluted H_2SO_4 and separated from the aqueous solution by careful neutralization with NH_3. The gasoline fraction boiling up to 125°C contains about 12 to 15 g/l pyridine, while the middle oil contains 42 to 56 g/l tar bases. Liquid-phase gasoline boiling up to 200°C contained, in one plant, 19 to 22 g/l light tar bases.

1(d) Aromatic compounds

Figure 13 shows the annual production of benzene from petroleum in the USA from 1950-1966, which demonstrates that since about 1958 a significant increase occurred. The liquid-phase product boiling up to 325°C contains about 50 wt% of aromatic compounds, depending on the aromaticity of the feed material and on the hydrogen partial pressure used. Additional to these "low"-boiling aromates, there are large concentrations of high-boiling polynuclear aromates and hydroaromates in those oil streams, like HOLD, boiling above 325 to 350°C.

The low-boiling aromates, such as benzene, toluene, xylene and ethyl benzene, which can constitute up to 40 wt% of the liquid-phase product, can be extracted in the same way as from reformer or hydroformer products. Suitable solvents are sulphur dioxide - propane mixtures or N-normalpyrrolidon solutions. The aromatic extract can be separated by distillation or decompression. The individual aromates can be separated by precision distillation. If toluene, xylene and ethyl benzene are not desired they can easily be converted by hydrodealkylation, as for instance in the Litol-Detol-or-Pyrosol process, to a very pure benzene. The equipment and the cost of operations are about the same as with the standard processes used in refineries for extracting and purifying aromatics. The starting material is,

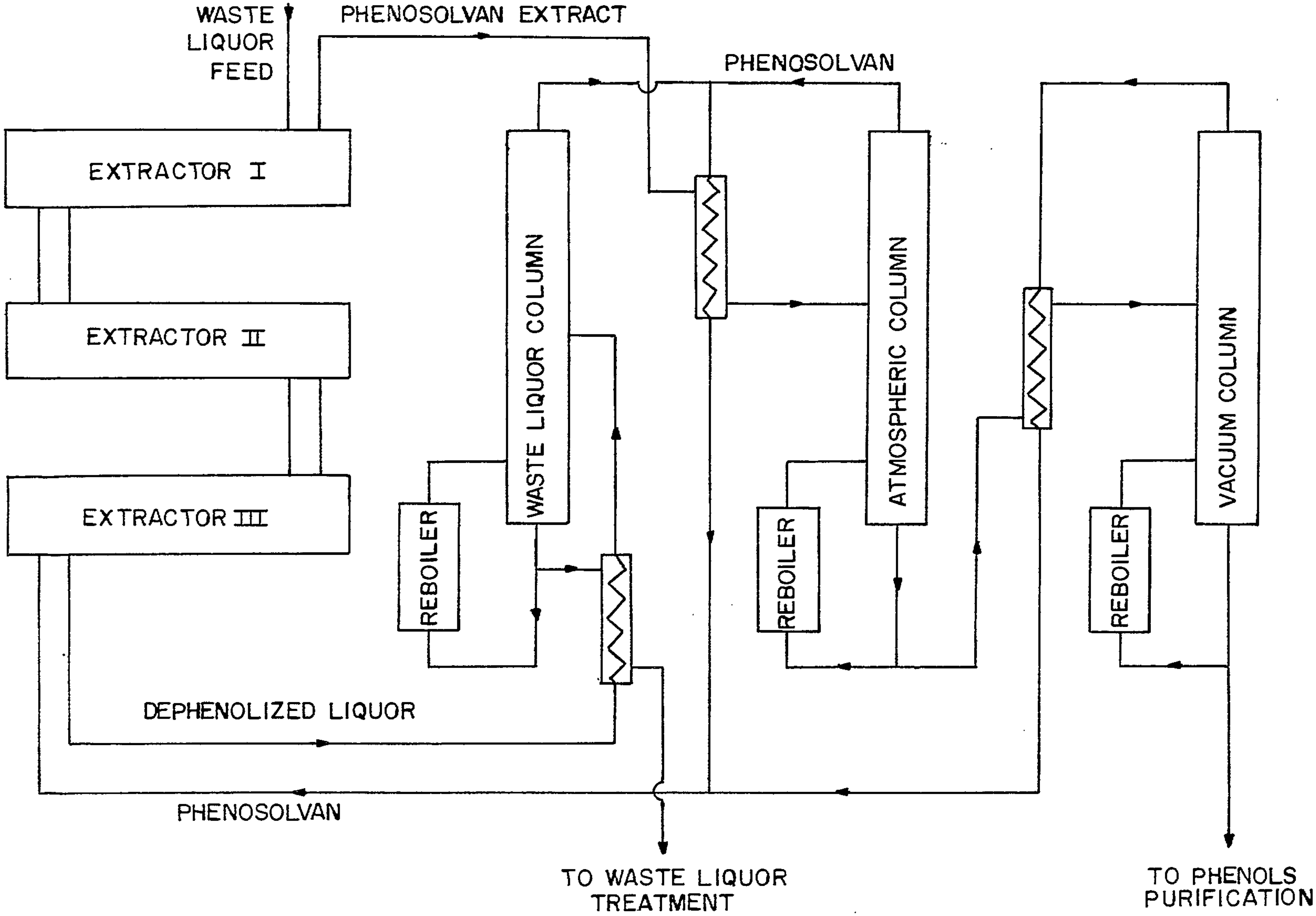

Figure 12. Phenol extraction from waste water.(11)

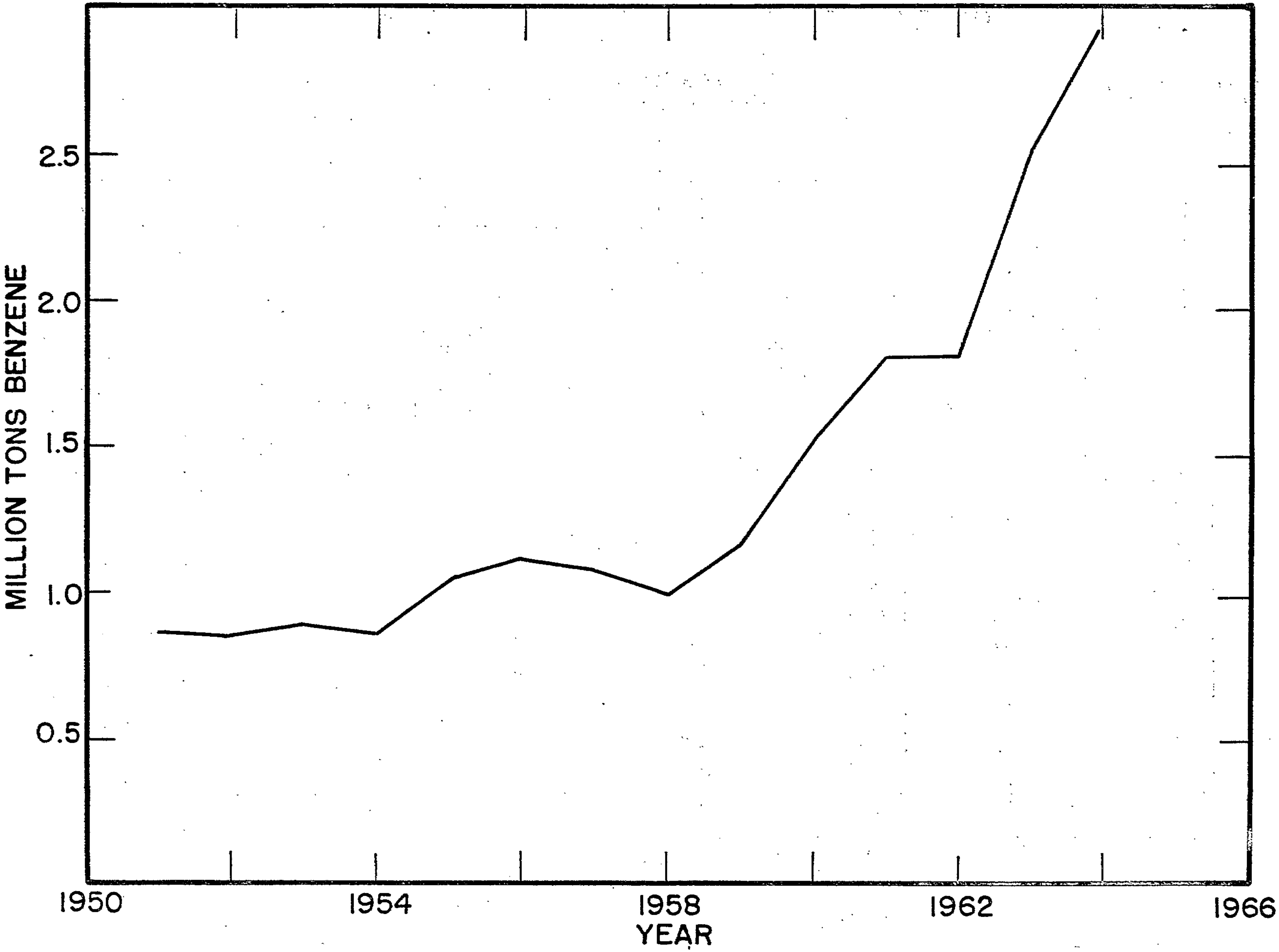

Figure 13. Production of benzene from petroleum in the USA, 1950-1966.(18)

however, considerably cheaper for not being charged with vapour phase, catalytic cracking, hydroforming or reforming costs.

Higher-molecular-weight polynuclear aromatics have not been recovered commercially, although their concentration in the heavy oils could reach, for instance, 10 to 12 wt% pyrene, 2.4 wt% 4-methyl pyrene, 1.2 wt% 4-9-dimethyl pyrene, 0.12 wt% 1-12 benzoperylene, 1.2 wt% coronene and 0.6 wt% carbazole(17). During the war, high-boiling aromatics had no priority and no extensive research was carried out and no new method was developed. The standard method of separating the high-boiling fractions of bituminous coal tar are, however, quite sufficient. They consist of obtaining narrow cuts by high-vacuum precision distillation, diluting the distillates with low-boiling paraffinic compounds ranging from pentane to hexadecane, or specific mixtures of them, cooling the mixtures, and centrifuging the precipitate. The precipitate has to be recrystallized repeatedly to obtain pure chemical compounds.

2. Chemicals from Processing of By-Products and Hydrogenation Off-Gases

In the hydrogenation of coal to liquid oils the large coal molecules have to be broken down to lower-molecular-weight hydrocarbons. In order to achieve a reasonably short residence time in this reaction, a certain percentage of the coal is broken down too far, namely, to the gaseous hydrocarbons methane to butane. Olefinic gases appear only to a negligible extent in the standard hydrogenation process. More olefines are obtained in the dehydrogenation processes, which operate at pressures from 10 to 50 at. and temperatures of 500 to 520°C. About 20 to 25 wt% of the carbon introduced with the coal appears in the hydrocarbon gases, distributed about equally among C_1, C_2, C_3, and C_4 hydrocarbons. These gases are dissolved in the liquid products and in the scrubbing oil. They are released in the let-down stages: first, down to about 10 to 14 at., the dissolved hydrogen, the methane and some ethane; then, in the next step, the rest of the ethane together with propane and butane. Another portion of the so-called rich gases comes from the distillation and the stabilization of the products, containing propane and most of the butane. With the exception of the stabilizer gas, all rich gases are scrubbed with alcazid lye and then, together with the stabilizer gas, with caustic. The gases thus cleaned are then separated at elevated pressure in precision distillation columns, or at low temperatures in the so-called Linde plants. The methane is combined with the lean-gas stream, and ethane and propane serve either as liquified petroleum gas or can be dehydrogenated to ethylene and propylene. The butanes are used as alkylation feed or are dehydrogenated to butene and isobutene. The pentane is added to the gasoline.

2(a) Ethylene and propylene

The ethane and propane portion coming from the Linde plant can be dehydrogenated at temperatures of approximately 602°C and less than atmospheric pressures of about 300 to 400 mm Hg(19). The reaction is endothermal and the heat for dehydrogenating the ethane-propane mixture is introduced either by heating the reaction tubes from the outside or by adding preheated oxygen to the preheated ethane mixture immediately before entering the reaction zone, which is filled with ceramic balls. The cracked gases are cooled in a heat exchanger to about 350°C and then by direct water-quenching to about 38°C, and caustic-scrubbed to remove organic acids and formaldehyde. The cleaned gas then passes through a hydrogenation reactor operating at atmospheric pressure and about 212°C, to eliminate the 0.5% acetylene formed simultaneously with the ethylene, by hydrogenating it with the hydrogen which is also formed during the reaction, over a nickel-chromium catalyst. The gases leaving this reactor have the composition: $H_2 + CH_4 + C_2H_2 + C_2H_6$, max. 5%, CO max 0.005%; H_2S, COS, O_2, CO_2, nil; remainder C_2H_4; and are separated and purified in various scrubbers and finally in a Linde plant, producing a gas with min 95% pure olefines. Ethylene and propylene are then ready for further processing to high V.I. lubricants and polymers or chemicals.

2(b) Butylene and isobutylene

The butanes from the Linde plant, if not used for liquified petroleum gases, can be dehydrogenated to butene and isobutene at about 571°C and atmospheric pressure over 8% chromic acid on Al_2O_3 with 1 to 2% alkali(20).

The butane feed preheated to 549°C by heat exchange, passes downward together with the catalyst pellets through tubes, heated from the outside to 571°C, at a rate of 680 m^3 per m^3 catalyst volume per hour. The catalyst is regenerated by burning the carbon from 3 to 4% down to 1 to 2% at about 571°C. It is charged and discharged to and from the regenerators and reaction tubes by means of automatic pocket valves, such that the catalyst retention time is about 4 hours in the reactors. The exit gas from the reactors is cooled to 25°C with water and then to 5°C with brine. The compounds liquified under these conditions represent the olefine feed stock for alkylation. It contains about 22 wt% butenes, 75.5 wt % n butane, and 2.5 wt% propane. The uncondensed portion of the reaction gas is washed with oil; it contains 80 to 85 vol % H_2 12-15 wt% CH_4 and 3 to 5 vol% C_2 hydrocarbons. The gas, stripped from the enriched wash-oil, is returned to the reactors.

Normal butane can easily be isomerized at 95°C and 18 at. over aluminum chloride-hydrochloric acid catalyst with ferric chloride as impurity. The conversion per pass is 25 to 30% and the ultimate yield is 95 to 97%.

Several processes for the conversion of butane and butene to butadiene are in use today. Butadiene can, for instance, be produced from n butene by oxydehydrogenation at about 420°C and atmospheric pressure with an upstream velocity of about 0.8 m/sec of the gases butene + air + steam. The conversion in the fluidized bed reactor was up to 50% per pass.

The methane and hydrogen formed in all the dehydrogenation processes are combined with the methane-hydrogen stream from the hydrogenation and can be used for the production of hydrogen by steam reforming. Acetylene from methane, as practiced in Germany during World War II, is more and more replaced by the cheaper ethylene as starting material.

2(c) Oxo chemicals

Since the liquid product contains an appreciable amount of higher molecular olefines, the latter, as well as those olefines obtained from the dehydrogenation of higher-boiling gasoline fractions and from the off-gases of the hydrogenation, can be reacted at moderate pressure and temperature with carbon monoxide and hydrogen to oxo-products(21).

ECONOMICS OF COAL HYDROGENATION WITH PRODUCTION OF CHEMICALS

The chemicals mentioned above are priced considerably higher than the liquid fuels that could be produced in the vapour-phase treatment in their place, and since their extraction is in many cases cheaper than the vapour-phase treatment, their recovery represents a sizable credit to the cost of operation of a coal hydrogenation. The olefines are manufactured in practically the same way as they are in standard refinery practice. The costs of feed materials for these dehydrogenation processes are, however, different. Since these feed materials represent a loss of starting material for either the refinery or the coal hydrogenation plant, they are mostly debited at the heating value of the starting material, i.e., either oil or coal at the price of natural gas. It then follows that, if the operating costs for equal processes are equal, and if the heat in coal is cheaper than in oil, it is more profitable to use the by-products from the coal hydrogenation.

The influence of the recovery of chemicals from the products and by-products of coal hydrogenation is also reflected in the 1952 cost estimates(10) of the U.S. Bureau of Mines (Ebasco and Bechtel) which stated that, from the total product revenue, 35.6% may come from aromatics and tar acids, 10.4% from ammonium sulphate and sulphur, and only 54% from motor fuels and LPG-gas. No production of olefines was included in these estimates, which are based on conventional plant design as used in Europe, with the exception that multi-shell reaction vessels were used instead of forged ones as in Europe.

CONCLUSION

Fuels and chemicals can be made from coal, by high-pressure hydrogenation, at prices competitive with those achieved by standard oil refining, if the price ratio of coal to petroleum remains as at present (1966) and if <u>all</u> the improvements developed after the war are incorporated in the operating scheme and equipment of the coal hydrogenation and if larger pieces of equipment are used to reduce investment, maintenance and heat costs.

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