THE ROLE OF OXYGEN IN THE PRODUCTION OF SYNTHETIC LIQUID FUELS FROM COAL

BY H. R. BATCHELDER, R. G. DRESSLER, R. F. TENNEY
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* * * * * * * * * **Report of Investigations 4775**

UNITED STATES DEPARTMENT OF THE INTERIOR
Oscar L. Chapman, Secretary
BUREAU OF MINES
James Boyd, Director

Work on manuscript completed November 1950. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is made: "Reprinted from Bureau of Mines Report of Investigations 4775."

March 1951

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ILLUSTRATIONS

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INTRODUCTION

Much information on oxygen production and the manufacture of synthetic liquid fuels has been published during the past several years. From time to time the investment and operating cost of oxygen plants of various sizes has been estimated. Surveys have been made so that the various processes by which oxygen is produced commercially might be compared. The gas-making processes in which oxygen is employed, which were used in Germany during the war, have been described in T.O.M. reels, and this information has been published. Descriptions of pilot-scale or proposed commercial plants for the production of synthesis gas or hydrogen and their conversion to synthetic liquid fuels also have been published. In general, each of these publications has dealt with a particular phase of the over-all problem. The present paper will discuss the relationship between these phases: The factors that affect oxygen manufacture and costs, the methods for the use of oxygen and for the production of synthetic liquid fuels, and, to some extent, the economic factors that must be considered.

SUMMARY AND CONCLUSIONS

The steps in the production of oxygen by the liquefaction and fractionation of air are discussed, together with the characteristics of the installations in this country for the production of oxygen.

The function of oxygen in the production of synthetic liquid fuels is primarily the gasification of coal with oxygen to produce mixtures of carbon monoxide and hydrogen, which then may be used directly, in the case of the Fischer-Tropsch synthesis, or as a source of hydrogen for coal hydrogenation. Among the potential advantages of the substitution of oxygen for air in the coal gasification step are the following: (1) Fuel economy, (2) increased capacity of equipment, (3) a wider range of possible fuels, (4) greater adaptability to pressure operation, and (5) a higher range of attainable temperatures.

The relationship of oxygen plant size to plant cost and to oxygen cost is discussed. Increases in oxygen cost are quite rapid as the size of the plant is reduced below about 400 tons per day.

The amount of oxygen necessary to produce synthetic fuel by Fischer-Tropsch is almost 700 pounds of oxygen per barrel of liquid. Under certain operating conditions for coal hydrogenation, this figure will be about 100 pounds of oxygen per barrel of fuel. Therefore, variations in oxygen cost will affect the cost of product from Fischer-Tropsch much more than from coal hydrogenation.

BASIC PROCESS STEPS IN THE MANUFACTURE OF OXYGEN BY LIQUID AIR FRACTIONATION

For the production of oxygen in tonnage quantities, the liquefaction of air and its subsequent fractionation has so far been considered the most suitable process. All commercial designs involve the following steps, which are basic in the process:

1. Supply of air into the plant apparatus.

Air is introduced into the plant process at one or more pressure levels. The minimum pressure for most of the input is governed by the operating conditions of the primary fractionating column. Higher pressures than this for some part or all of the input may be used for the expansion differential to provide refrigeration for the process. A small auxiliary stream is often arranged to assist in keeping impurities from fouling the heat exchangers and is usually utilized as a refrigerating medium. The higher the pressure of this stream, the less differential is needed in the main air supply above the primary column.

2. Refrigeration of the apparatus: This must be adequate to start a warm plant in reasonable time and to absorb all atmospheric heat penetration and all heat residues from the temperature differences between ingoing air and outgoing products.

Refrigeration is produced in each design by the expansion of some gas in the system (usually a portion of the ingoing air supply) after this gas has been compressed and cooled. Expansion may be through a simple throttling valve, but usually part or all of the medium is put through an expansion machine, engine, or turbine, connected to an electric generator or water pump to get the greater cooling effect from the work performed and as source of power recovery. An auxiliary power-driven refrigerating machine frequently has been used for pre-cooling the refrigerating side stream to freeze out moisture and also to yield a lower temperature in the expanded stream.

3. Heat transfer between ingoing air and outgoing products to minimize the admission of heat to the process and thus reduce the refrigeration requirements.

When operations are stabilized, cooling of the ingoing air supply and warming of the outgoing products are the first and last stages, respectively, in the design flow. In every case, simple but highly efficient units for the transfer of this heat are sought to reduce the refrigerating requirements of the plant. It was the development of the Frankl-type regenerators and the more recent countercurrent-flow heat exchangers that has made economical bulk plants possible. In both these types the ingoing air is cooled nearly to its liquefying temperature at the fractionating-column pressure. The regenerators are pairs of shells packed with heat-absorbing metal in a form to offer a large surface. Nitrogen or oxygen product passing outward through one of the pair absorbs the heat from the packing and is itself warmed nearly to atmospheric temperature, whereas air flowing through the alternate shell has its temperature reduced by transfer to the previously cooled packing. The more recently developed heat exchangers have parallel contiguous passages, the ingoing air through one giving up heat to the product gas going out through the other. The plant design also includes other heat exchangers of the countercurrent-flow type, in which small transfers are made at the lowest temperature levels between the outgoing products as they leave the upper column and the reflux liquids entering the column.

4. Removal from the air supply of impurities, which interfere with later operations.

Dust as well as moisture, carbon dioxide, and other more minute impurities that may solidify and clog the columns and auxiliary lines are removed from the ingoing air. Solid particles are taken out by filtering or washing the air before entrance to the air supply unit or in the first stage of air aftercooling. Substantially all of the moisture, carbon dioxide, and other crystallizable impurities if not removed from the inlet air supply by gel adsorption are deposited during the initial stages of cooling in the primary heat exchangers. Reversal of the flows through the pairs of regenerators or the heat exchangers lets the outgoing product gas pick up the impurities from these passages. Where ingoing air has several times the pressure of the outgoing product, the much larger outgoing volume is effective in removing all the deposit from the previous half cycle. When pressure differentials are small, the outgoing gas is not so effective, even with some excess product from the auxiliary air supply, to clear the passages completely. Periodical thawing of these becomes necessary, and some interruption in production must be arranged. Auxiliary air inputs treated outside the primary heat exchangers are purified by refrigeration and chemical means, moisture being removed by compression and cooling to freezing temperature or by adsorption in gel driers, and carbon dioxide by caustic scrubbing.

5. Fractionation of liquefied air into component nitrogen and oxygen and delivery of both of these as product gases.

The rectifier for this fractionation is almost universally a double column, the upper section of which operates slightly above atmospheric pressure and the lower section at 60 to 70 p.s.i.g. Dividing the two sections is a heat exchanger in which nitrogen overhead from the lower column is condensed and supplies the heat to reboil the oxygen bottoms in the upper section. It is this combination duty that sets the pressure differential between the two sections. The oxygen bottoms in the low-pressure section will be at a temperature of perhaps -294° F. when the condensed nitrogen in the high-pressure section is at a temperature of -290° F. This small difference under the excellent conditions for heat transfer and the relatively large transfer surface is enough to permit the exchange of the necessary heat.

The partly liquefied incoming air enters the lower section, in which it is fractionated into an oxygen-rich bottoms and a relatively high-nitrogen overhead. Part of the nitrogen condensed in the heat exchanger is returned to the top tray as reflux. The bottoms from the high-pressure column usually are fed to about the center of the upper section, together with any low-pressure air that is being used. The separation is made in this section between substantially specification-purity oxygen bottoms and a product nitrogen overhead. Reflux for this upper section also is the condensed overhead from the lower section.

The liquid oxygen drawn off from the reboiler is vaporized to give gaseous product oxygen. The evaporation of this material supplies some refrigeration, usually to an auxiliary stream, and the evaporated product passes into the regenerators or exchangers described above. The gaseous nitrogen leaves the rectifier from the top of the secondary column to go out through its series of heat-transfer apparatus.

The cycle developed by the Elliott Co. involves some modification of the fractionating column but the principles remain essentially the same.

6. Removal of acetylene.

The presence of acetylene in significant concentration in liquid oxygen involves the hazard of explosion. The range of stability appears to be limited to the amount of acetylene soluble in the liquid oxygen. Beyond that, undissolved crystals are formed and apparently are unstable. Several methods of minimizing this hazard are employed. For the minute quantities of acetylene in nonindustrial atmospheres, which may be carried beyond the input air-cooling apparatus, the maximum concentration occurs in the liquid-oxygen vaporizer as the last portion of the oxygen liquid is evaporating. Retention of the last 1 percent of oxygen in the liquid form at the end of this evaporation and its withdrawal before further concentration keep the acetylene within the acceptable limits. Chemical tests of the liquid thus discharged are made to confirm the adequacy of this procedure. In more modern, large-scale plants where higher acetylene content is anticipated in the input air, or the loss of liquid oxygen would be important, acetylene is removed from the liquefied air before the fractionating column by gel adsorbers. These are revivified by streams of heated air or nitrogen, and control tests are made on this gas stream for the acetylene quantity thus removed.

TYPE AND SIZE OF COMMERCIAL PLANTS IN THE UNITED STATES

The design of the large plants in this country has developed largely from those constructed in Germany for steel plants, hydrogenation, synthesis and other chemical industries. These German plants, substantially all of which were designed by Linde, had a maximum capacity of 150 tons per day per unit, and larger installations were composed of multiples of those units. It is understood that a 20-unit plant was projected during the war, and 12 of the units actually were installed. Other 12-unit plants were constructed at several places. The design of these plants became standardized on the double-column rectifier, with the main air input at 60 p.s.i.g. from turbine compressors and the air purified and cooled in the Frankl-type regenerators. The auxiliary air stream (7 percent) was compressed to 3,000 p.s.i.g., caustic-scrubbed, and dried and cooled by amonia refrigeration. This stream, after further cooling, was expanded through a throttling valve into the pressure column to produce liquid air. A part of the uncondensed nitrogen from the top of the pressure column was put through turbine expanders to produce efficient refrigeration and some power recovery. Acetylene removal in these plants was effected by withdrawing the last 1 percent of oxygen liquid unevaporated. It appears that some wartime restrictions may have prevented the use of gel adsorbers, as those had already been installed in some smaller plants. The standard product of these large-scale plants was 98 percent oxygen.

The 24-ton-per-day Linde-Frankl plant transferred from Germany and re-erected in the Synthetic Fuels Plant at Louisiana, Mo., embodies most of the standard Linde design features of the large German plants. It uses, however, reciprocating compression for the second stage of air input, expansion of part of the h.p. auxiliary air through working expansion engines, delivery of all nitrogen from the lower into the upper column as liquid, and introduction of some 20 percent of the air through the oxygen-cooled regenerators directly into the secondary column at the primary stage pressure (12-13 p.s.i.g.). An auxiliary column is superimposed on the rectifier for the recovery of some 5 percent of the input air as pure nitrogen (0.5 percent O_2) for special purposes.

Transfer of the Linde design to this country also has been indicated by recent reference[4] to a 200-ton-daily-capacity gaseous oxygen pilot plant built

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[4] Chemical Engineering Progress, vol. 43, No. 7, July 1947, News Section, p. 16.

by Linde Air Products Co. for development purposes and put into operation late in 1946 at East Chicago, Ind. The brief description in the editorial report containing this reference implies the conventional Linde cycle, using the double-column rectifier, the Frankl regenerators for heat exchange and removal of most of the water vapor and carbon dioxide, delivery of part of the air to the lower column, and expansion of the remainder in a work turbine for refrigeration. Air supply is at 80 p.s.i.g. to operate the lower column at 75 p.s.i.g. and the upper column at 5 p.s.i.g. Product is 90-95 percent oxygen. A thawing period each 30 to 60 days is implied.

The first of the large-scale industrial plants in this country appears to have been the Koppers-Air Reduction Co. installation in the Bethlehem Steel plant at Johnstown, Pa., with a capacity of 130 tons per day, which was put in operation during 1948. This continues the use of the Frankl regenerators, the double-column rectifier, and the chemical purification of the auxiliary air input. This auxiliary air, together with part of the main air input, is expanded through turbine-type expanders for refrigeration of the process. The expanded air goes into a nitrogen column working at an intermediate pressure and discharging uncondensed nitrogen through another turbine expander for additional refrigeration. All liquefied air is filtered, and acetylene is removed from it by passage through gel adsorbers, which are revivified by an auxiliary nitrogen stream.

The Hydrocarbon Research-Stacy Dresser plant of the McCarthy Chemical Co. at Winnie, Tex.[5], is rated to produce 175 tons per day of 95 percent oxygen and was started in January of 1949. The double-column fractionation is continued, using bubble cap decks, but the cooling-purifying air regenerators have been replaced by specially designed heat exchangers for the same dual purposes. In one set of these the air and nitrogen and in the other the air and oxygen flow countercurrently through contiguous passages, the flows being reversed at intervals, so that air impurities deposited are removed by out-going products. A bleed-stream of air from the exchanger outlets is passed back through a third, nonreversing passage in each exchanger to give extra cooling against the incoming air and maintain constant temperature differentials in the exchangers and more effective removal of impurities. This side stream is thus warmed slightly and then, for refrigeration of the plant, is put through the expansion turbine, which does work in pumping plant-cooling water. Plant air supply is compressed in gas-driven reciprocating units to 85 p.s.i.g. No chemical purification of air is included. Acetylene is removed by silica gel adsorption. Latest report since starting has indicated no thawing or deriming yet necessary.[6]

Other commercial-size plants, the construction of which has been announced or is under way, include:[6]

Hydrocarbon Research - Foster Wheeler plant for Carthage Hydrocol Co. at Brownsville, Tex. Two 1,000-ton-per-day units for synthetic gasoline and oil production from natural gas.

Air Products Inc., for Wierton Steel Co. at Weirton, W. Va.; 400-ton-per-day unit for metallurgical processes.

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[5] Bludworth, J. E.: Petroleum Processing, vol. 4, No. 4, April 1949, pp. 377-9.

[6] Wright, C. C., Current Status of Tonnage Oxygen; American Gas Association Subcommittee Report, May 1949.

Linde Air Products at E. I. du Pont de Nemours synthetic ammonia plant at Belle, W. Va.; 360-ton-per-day unit for hydrogen production.

Linde Air Products at Wheeling Steel Corp., Steubenville, Ohio; 135-ton-per-day unit for metallurgical processes.

COST OF OXYGEN

The size of an oxygen unit has considerable influence on the cost of the product. This is shown in figure 1, which was drawn from data from several published sources[7/][8/] and some private sources, but principally from the American Gas Association report.[6/] The costs reported there were based upon the following:

Operation - 24 hours per day, 365 days per year.
Steam - $0.40 per 1,000 pounds.
Cooling water - $0.01 per 1,000 gallons.
Electricity - $0.005 per kw.-hr.
Labor - 48 man hours per day at $1.40 per hour.
Maintenance and supplies - 1.5 percent of plant cost per year.
Fixed charges - 10 percent of plant cost per year.

No credit for byproduct N_2 or for side stream of 99.5 percent O_2.

This report is considered to be the most comprehensive published survey of oxygen plants and costs to date. The costs from earlier sources have been adjusted to 1948 levels by application of a factor.

All the processes shown, with one exception, are in reasonably good agreement as to the relation of plant capacity and production cost. The data given by one company were about 40 percent below the average of the other values reported and have not been included. Referring to the graph, a 300-ton-per-day plant would produce oxygen at about $4.80 per ton. If the plant capacity were 100 tons per day, the cost would be almost $7 per ton, and if the capacity were increased to 1,000 tons per day, the cost would be reduced to $3.50 per ton.

The variation in the cost of the oxygen with the size of the plant is, of course, due primarily to the fact that the investment cost and fixed charges do not increase proportionately as the plant capacity is increased, and that the amount of operating labor for almost any plant of normal size is substantially the same, so that the labor charge per unit of oxygen is decreased in proportion to the size of the plant. The utilities, such as steam, electricity, and cooling water, are, in general, a constant charge per unit of oxygen regardless of plant size.

The information available upon the estimated investment cost for oxygen plants does not agree as well as that available on the cost of the product. In figure 2 is given a curve showing the relationship between plant cost and capacity. The line represents approximately the average of costs given by various sources for plants of each size. This would indicate investment costs of $1,250,000, $2,380,000, and $4,500,000, respectively, for the 100, 300, and 1,000-ton-per-day plants discussed above.

[7/] Downs, C. R., Impact of Tonnage Oxygen on American Chemical Industry: Chem. Eng., vol. 55, No. 8, August 1948, p. 113.

[8/] Gas Age, Apr. 4, 1946.

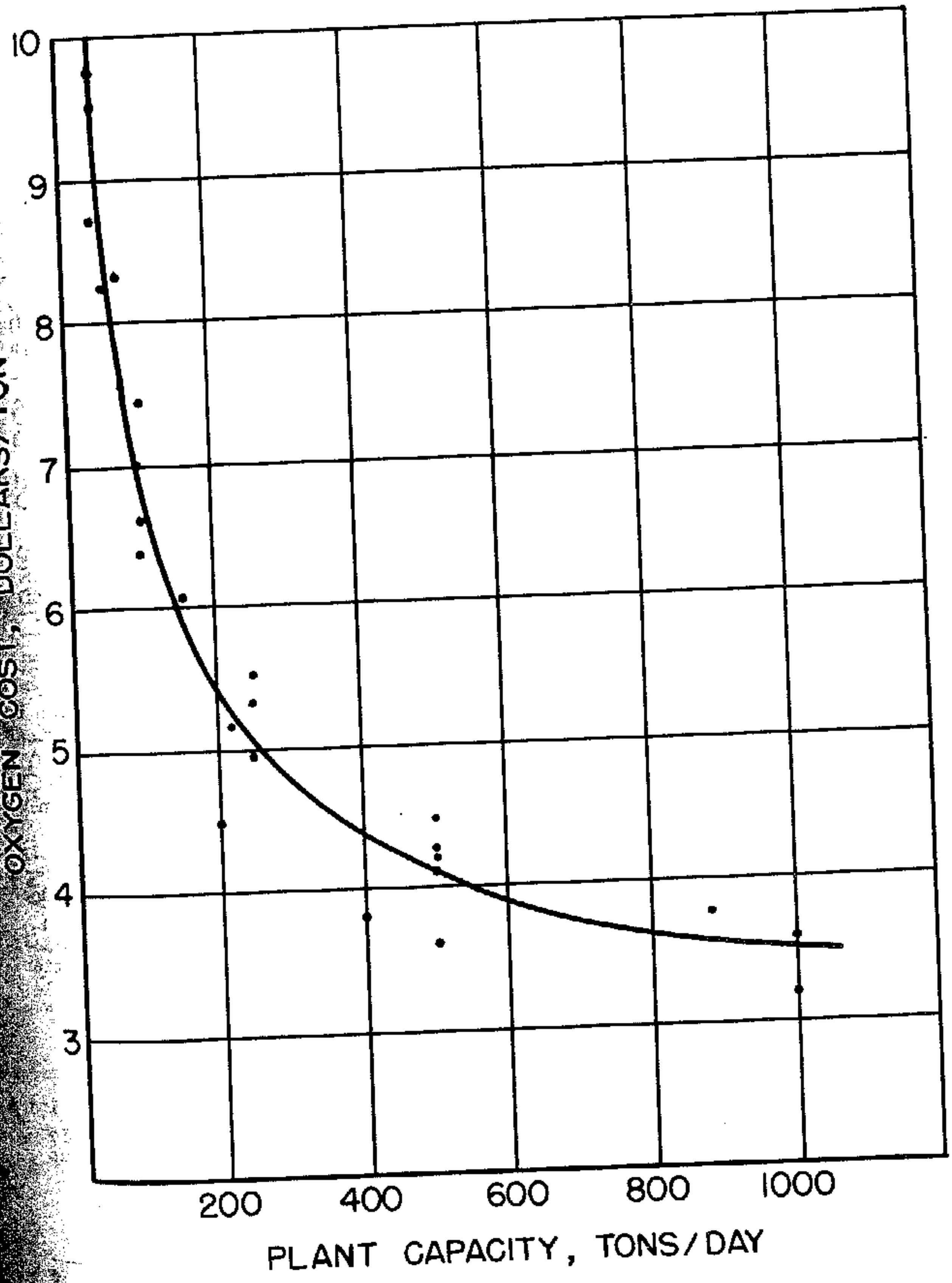

Figure 1. - Effect of plant capacity on the cost of oxygen.

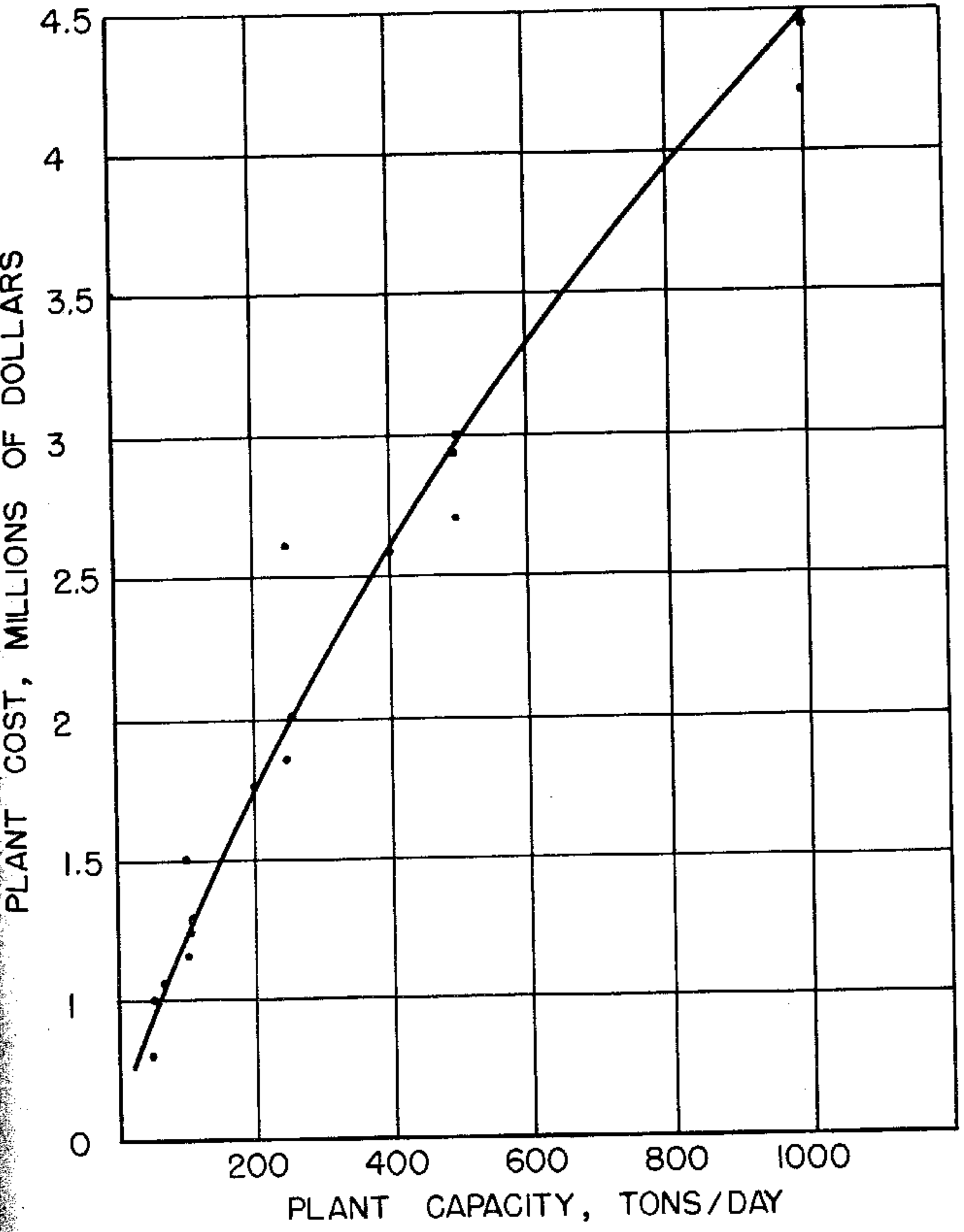

Figure 2. - Effect of oxygen plant capacity on the plant cost.

SYNTHETIC FUEL PROCESSES DEPENDING ON OXYGEN

Coal Hydrogenation

The first commercial plant for making gasoline from coal was built at Leuna, Germany, and was put into operation in 1926. Subsequently, at least 10 other plants were built in Germany to convert such raw materials as brown coal, bituminous coal, pitch, etc., into high-grade motor fuel. The bulk of Germany's aviation gasoline in World War II was made by the hydrogenation process. England also constructed two such plants. The first, for bituminous-coal hydrogenation, was completed in 1935.

This process consists essentially of splitting the large molecules of coal or other raw materials and adding hydrogen directly to the loose ends of the resulting smaller molecules. The lighter products thus formed are much richer in hydrogen than the raw material. High pressures, from 1,000 to 10,000 p.s.i.g., and temperatures of 750° F. to 1,000° F. are required in the reaction, in addition to a suitable catalyst, to obtain practical conversions. For coal and materials having a boiling point above approximately 650°F. the reaction is carried out in the liquid state with the catalyst added to the feed. For lighter feed stocks, a fixed catalyst bed is generally used, and the reaction is carried out in the vapor phase. Recent work[9][10] indicates the possibility of using the fluidized technique to replace the liquid-phase operation. At least two stages of hydrogenation are required if gasoline is the desired product. The process is characterized by at least three features: (1) The wide range of products obtainable, such as LP-gas, gasoline, jet fuel, Diesel fuel, distillate fuels, or residual fuel oils, (2) and products that retain some characteristics of the original raw material, and (3) the almost complete conversion of all process coal to hydrocarbons.

Hydrogen requirements for this process may vary considerably, depending on the available hydrogen in the feed material and on the end products desired. When gasoline is produced as the primary product from bituminous coal, a typical process balance[11] shows the hydrogen requirement to be 8,000 cubic feet per barrel of liquid product.

The purity of the hydrogen is not critical, 95 to 98 percent being the usual range. Carbon monoxide is normally limited to 0.15 percent for vapor-phase operations.

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[9] Chemical Engineering, vol. 56, No. 7, July 1949, p. 67.

[10] Clark, E. L., Pelipetz, M. G., Storch, H. H., Weller, S., Schreiber, S., Hydrogenation of Coal in a Fluidized Bed: Presented before the Gas and Fuels Div., Am. Chem. Soc., 116th. meeting, Atlantic City, N. J., September 18-23, 1949.

[11] Hirst, L. L., Markovits, J. A., Skinner, L. C., Dougherty, R. W., and Donath, E. E., Estimated Plant and Operating Costs for Producing Gasoline by Coal Hydrogenation: Bureau of Mines Rept. of Investigations 4564, August 1949, p. 32.

The normal hydrogenation plant, using coal as the only raw material, is able to recover 15 to 20 percent of the total hydrogen requirement from its own residue gas, hydrogen which was dissolved in the oil streams at high pressure and subsequently released during pressure reduction. A low-temperature separation plant is usually included for this purpose as well as to purge nitrogen from the system. The hydrocarbon tail gases, methane and ethane, may be reformed with steam to yield an additional 40 to 65 percent of the hydrogen required. The volume of hydrogen produced would be reduced by about one-third if partial combustion with oxygen is used.

The mixtures of carbon monoxide and hydrogen resulting from reforming must be treated with steam over a catalyst to convert the carbon monoxide to dioxide with the production of an equal volume of hydrogen. The carbon dioxide is then removed by scrubbing. This step is necessary in producing hydrogen by almost any gasification process.

The balance of the hydrogen requirement, amounting to 20 to 50 percent of the total, must then be made directly from outside raw materials. In the bituminous-coal example cited above, approximately 3,500 cubic feet of the 8,000 cubic feet total per barrel would need to be produced in this manner.

As far as the process itself is concerned, the source of this additional hydrogen is immaterial. In Germany, under the then existing economy and wartime conditions, many sources of hydrogen were used. However, most of these would not be feasible for a full-scale synthetic-fuels industry either by reason of practicality, considering the magnitude of the operations, or economy. Under normal circumstances it is anticipated that the gasification of solid fuels probably would be the major source of the required gas. In a subsequent section, various means of gasifying solid fuels are discussed, and the conclusion is drawn that the direct reaction of coal with oxygen and steam has many potential advantages.

Gas Synthesis (Synthesis Gas from Coal)

The Germans began their work on the Fischer-Tropsch synthesis (synthine process) on an industrial scale in 1935. Especially since World War II, efforts in the United States have been directed toward the use of iron catalysts as being more economical and readily available than cobalt and toward the increase in unit plant capacity by means of improved heat transfer. Virtually all of the major oil companies, some of them in conjunction with coal interests, are occupied in this development work. In general, they have confined their work to the application of the fluidized-bed technique. The Bureau of Mines has developed, on a pilot scale, a fixed-bed type of reaction in which the heat is removed by circulation of a coolant oil in which the catalyst bed is submerged.

A mixture of hydrogen and carbon monoxide is passed over an activated iron catalyst at temperatures of 500° to 600° F. and pressures in the neighborhood of 300 p.s.i. From this reaction, a range of synthetic liquid fuels and organic chemicals is produced. The ratio of hydrogen to carbon monoxide used is normally in the range 1.3:1 to 2:1. The gas must be thoroughly purified of sulfur compounds to protect the catalyst.

The synthesis gas (about 30,000 cubic feet is required per barrel of product produced) may come from several sources. Using oxygen, the gas may be made from either coal or natural gas. From a large-scale viewpoint, and in the interest of conservation, we must be concerned principally with the production of this gas from coal. Because natural gas is cheap and plentiful in some areas, and because its conversion to synthesis gas offers fewer difficulties than coal, it is an attractive starting point for commercial operations. Reference is made to the plant being built by Carthage Hydrocol[12][13] at Brownsville, Tex., which is being designed to use 40,000,000 standard cubic feet per day of oxygen to convert 64,000,000 cubic feet of natural gas into carbon monoxide and hydrogen. This is to be accomplished at 2,400° F. or above and at 250-300 p.s.i.g.

Using coal as a basic raw material, many operations for the production of synthesis gas or hydrogen have been conducted in the past as a two-step process. The coal is first coked in conventional ovens, usually with the recovery of byproduct liquids and gas. The coke thus formed is caused to react with steam, usually in a blue-gas set. This involves relatively high investment costs and the necessity for a good coking coal. One of the more attractive possibilities which cheap tonnage oxygen opens up is that of gasifying the coal directly in continuous processes using oxygen and steam.

Several projects directed toward the development of processes to gasify coal with oxygen and steam are currently being carried on by private or Government groups. At Trail, British Columbia, the Consolidated Mining & Smelting Co. of Canada operates a more or less standard producer using an oxygen-steam blast instead of the conventional air-steam blast.[14]

The Standard Oil Co. (N.J.) and the Pittsburgh Consolidation Coal Co. announced in 1947 joint plans for a $300,000 gasification demonstration-size pilot unit at Library, Pa.[15]

The Bureau of Mines at Morgantown, W. Va., also has a large pilot unit operating with powdered coal, oxygen, and steam. The unit is designed for minimum usage of oxygen by substitution of high-temperature steam (up to 3,500° F.), superheated by two Royster stoves operating alternately.[16] Also, at Pittsburgh, the Bureau operates an oxygen-coal pilot unit designed on the vortex principle.

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[12] Keith, P. C., Gasoline from Natural Gas: Oil and Gas Jour. vol. 45, No. 6, June 15, 1946, p. 102.

[13] Latta, James E., and Walker, Scott W., Stanolind Oil & Gas Co., Commercial Application of Hydrocarbon Synthesis in the United States: Chem. Eng. Progress, vol. 44, No. 2, February 1948, p. 173.

[14] Wright, C. C., Barclay, K. M., and Mitchell, R. F., The Production of Hydrogen and Synthesis Gas by the Oxygen Gasification of Solid Fuels-Consolidated Mining and Smelting Company of Canada: Ind. Eng. Chem., vol. 40, No. 4, April 1948, p. 592.

[15] Bland, William F., Gasification of Coal May Foreshadow New Industry Replacing Oil Refineries: National Petroleum News, vol. 39, No. 14, April 2, 1947, p. 23.

[16] Schmidt, L. D., McGee, J. P., and Slone, M. C., A Pilot Plant for Gasifying Powdered Coal Entrained in Oxygen and Steam: Chemical Engineering Progress, vol. 44, No. 10, October 1948, p. 737.

The Bureau of Mines Synthetic Fuels Demonstration Plant at Louisiana, Mo., has a complete gas-synthesis demonstration plant under construction.[17] At this time the oxygen plant is operating on a production basis. The coal-gasification unit is operating intermittently for experimental purposes. The purification, synthesis, and distillation units are still under construction.

The methods used in Germany for the production of synthesis gas or hydrogen by means of oxygen from coal or coke are surveyed in a paper by L. L. Newman.[18]

POTENTIAL ADVANTAGES OF OXYGEN GASIFICATION

It has been shown in the foregoing that the use of oxygen in the production of synthetic fuels is primarily a question of the gasification of coal to produce hydrogen for coal hydrogenation or carbon monoxide-hydrogen mixtures for Fischer-Tropsch synthesis.

In a coal-gasification process, heat must be supplied to drive off and decompose the volatile components of the fuel and to support the endothermic reaction between carbon and steam. This may be supplied internally by partial combustion of the fuel with oxygen, by intermittent combustion with air to store heat in the fuel bed, or by the application of external heat.

The use of oxygen in place of air or external heating of the gasification vessel may show one or more of the following five advantages: (1) Fuel economy, (2) increased capacity of equipment, (3) a wider range of possible fuels, (4) greater adaptability to pressure operation, and (5) a higher range of attainable temperatures. These will be discussed in turn.

1. Fuel economy.

On a theoretical basis, with perfect combustion and perfect recovery of waste heat, there would be substantially no difference between burning carbon with air to carbon dioxide to supply the heat necessary for the reaction of carbon with steam to form carbon monoxide and hydrogen on the one hand, and, on the other, the partial combustion of carbon with oxygen to form carbon monoxide, again to supply the heat necessary for the reaction of carbon and steam. On the basis of a given volume of synthesis gas produced, the carbon requirements would be substantially the same for the two methods of operation. However, in the absence of perfect combustion and heat recovery, there is a substantial fuel economy to be achieved by the use of oxygen. The volume of nitrogen that must be pumped, heated, and cooled in an air-blown process is a major burden on the efficiency of the process.

LIMITING OXYGEN PRICE DOLLARS / TON

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[17] Hirst, L. L., Markovits, J. A., Dressler, R. G., and Batchelder, H. R., The Bureau of Mines Demonstration Plants in the Synthetic Fuels Picture: Proceedings of American Gas Association for 1948.

[18] Newman, L. L., Oxygen in the Production of Hydrogen or Synthesis Gas: Ind. Eng. Chem., vol. 40, No. 4, April 1948, p. 559.

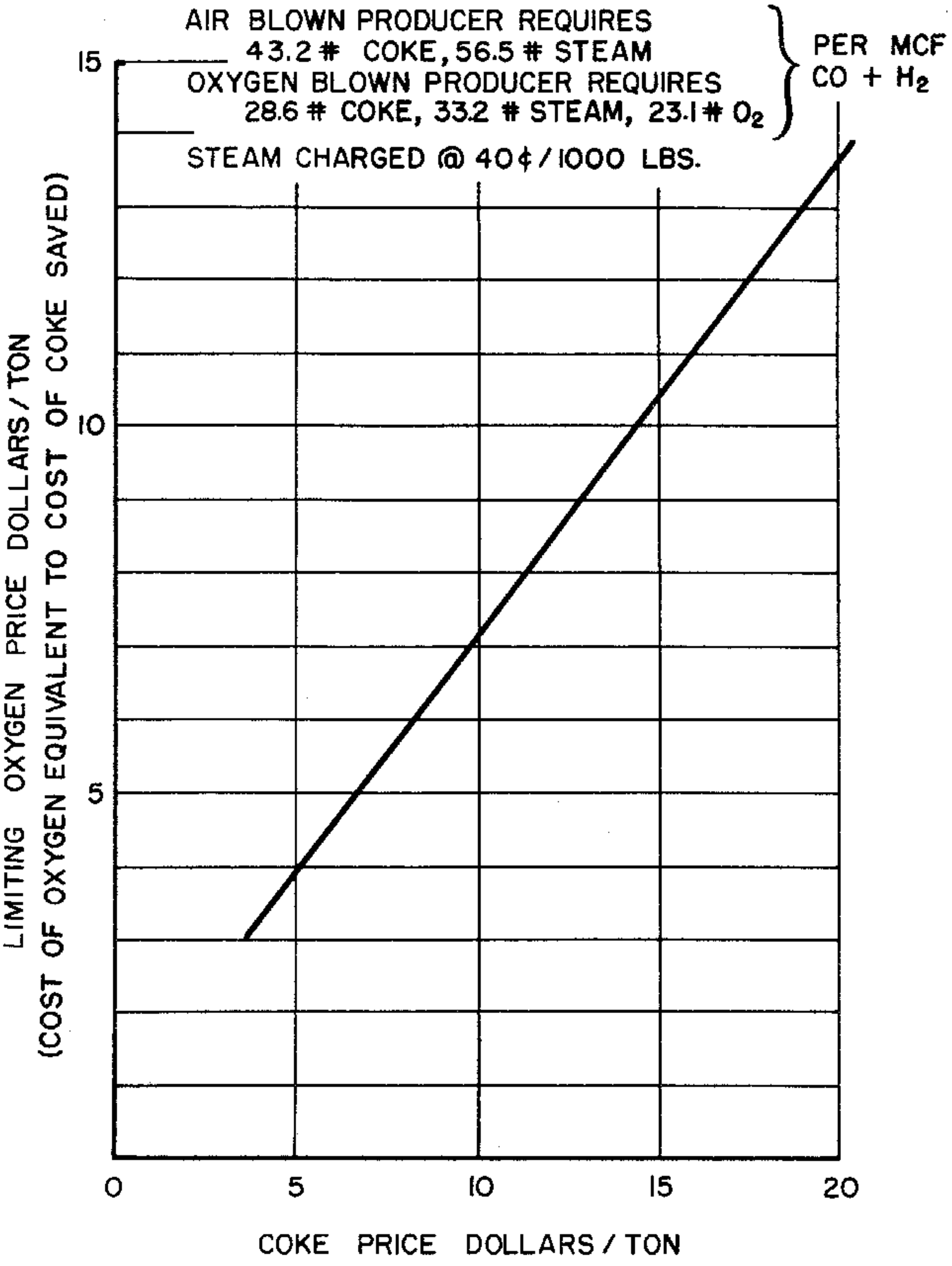

Figure 3. - Comparison of coke-air and coke-oxygen operations (variations of limiting oxygen price with coke price).

Direct comparisons between oxygen and air-blown operations are not too common. The operation of a Wellman-Galusha producer with coke and oxygen at Trail, British Columbia, was reported by Wright, Barclay, and Mitchell.14/ In this paper, comparison was drawn between the operation of the producer on sized coke and that of a standard blue-gas set. There it was stated that 23.5 pounds of carbon, 23.1 pounds of oxygen, and 33.2 pounds of steam were required to produce 1,000 cubic feet of carbon monoxide and hydrogen in the producer. In a blue-gas set, 35.5 pounds of carbon and 36.5 pounds of steam were required to produce 1,000 cubic feet of carbon monoxide plus hydrogen, using air blast. Disregarding the power consumption of the air blowers and making constant allowance for the cost of steam, comparison can be made, then, of the oxygen price that will allow a break-even operation as a function of the price of coke. This relationship is shown in figure 3. From this it will be seen that with coke at $5 a ton, an oxygen price below $3.95 per ton would allow some advantage to be shown for the oxygen-blown operation. If the coke price is $10 per ton, then any oxygen price below approximately $7 per ton would show an advantage for the oxygen-blown operation. Obviously, as the chief effect of the use of oxygen is saving fuel, the more expensive the fuel the higher the price that can be justified for oxygen or the greater saving is shown at a given price of oxygen. From this curve, also, it can be seen that if a minimum achievable price of oxygen is $3 per ton, then the use of oxygen cannot be justified on this basis when coke is less than $3.50 per ton.

(Since the foregoing was written, the oxygen-blown producer installed at the Gas Synthesis Demonstration Plant at Louisiana, Mo., has been operated to produce synthesis gas from coke, steam, and oxygen. A lower oxygen usage was achieved here then that reported by Wright, Barclay, and Mitchell. This changes the relationship somewhat; for example, with a coke price of $10 per ton, an oxygen price up to $8.50 per ton would show an advantage for the oxygen-blown operation.)19/

It is recognized that coke is not, perhaps, the ideal fuel for gasification, as its use involves appreciable investment in coke ovens and as it is a relatively high-cost fuel. The comparison is made here on the basis of the coke, primarily because there are no data on commerical operations on any other basis.

It should be recognized, however, that the same general relationships will prevail when suitable processes for the gasification of coal with either oxygen or air are developed, and the magnitude of the saving to be achieved by the use of oxygen will be a function of the price of the fuel that has been saved.

19/ Batchelder, H. R., Dressler, R. G., Tenney, R. F., Kruger, R. E., and Segur, R. D., Operation of Korpely Producer with Oxygen-Enriched Blast: Presented at the Annual Meeting of the American Gas Association in Atlantic City, N. J., Oct. 4, 1950.

2. Increased capacity of equipment.

As coke is substantially the only fuel readily adapted to both oxygen and air-blown operations, again the comparison between the two processes to illustrate the increased capacity achievable with oxygen must be made between the blue-gas set and the oxygen-blown producer. Referring again to Wright, Barclay, and Mitchell[14], the authors found that the producer at Trail could achieve gasification rates up to 5,750 pounds of coke per hour. They state that the capacity was limited by the equipment for feeding the coke and by the size of the gas offtake line. They stated their belief "*** very much higher rates are entirely feasible if desired." On the basis of this throughput and 23.5 pounds of coke per M c.f. of gas, the production was about 245 M c.f. per hour in this unit. A blue-gas set of the same internal diameter (10 ft. I.D.) should produce, on normal operation, about 200 M c.f. per hour.

From these figures it can be seen that at least a 25 percent improvement in output was achieved, and all of the evidence indicated that a very much higher rate on the producer could have been realized.

(More recently, the operation of a modified blue-gas set with oxygen has been reported by Blatchford.[20] The throughputs achieved in this operation were appreciably higher than the maximum at Trail. Gasification rates as high as 475 M c.f. per hour were achieved, which is well over twice the capacity of a blue-gas set on air operation.)

Comparing the producer at Trail, operating on lump coke, with the preliminary operations of the powdered-coal gasifier installed in the Bureau of Mines plant at Louisiana, Mo., it can be shown that, on the basis of equal reaction volumes, the powdered-coal gasifier produces approximately 50 percent more than the producer at Trail actually did. The design capacity for the powdered-coal gasifier is approximately twice that actually achieved in the Wellman producer.

3. Wider range of possible fuels.

Any gasification of solid fuels without the use of oxygen must depend on intermittent air blowing, circulation of heated fuel from a combustion to a gasification zone, or the application of external heat to the gasification vessel. In substantially all of these, coke or nonagglomerating coal is indicated because of the potential difficulty with sticking and coking. In an intermittent air-blown operation, of which the blue-gas set is the best example, coke is standard practice, and the attempts to use bituminous coals in general introduce tar and oils into the gas and substantially reduce the capacity. In the processes involving the circulation of heated fuel, such as have been variously proposed for fluid-bed gasification, a precarbonizing step has usually been included because of the obvious difficulties with coking coals in such an operation. This, in general, applies also to the fixed or slowly moving beds of fuel to which external heat is supplied for the gasification reaction.

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[20] Blatchford, J. W., The Production of Water Gas with Tonnage Oxygen: Presented at the Production and Chemical Conference of the American Gas Association at New York, N. Y., May 22-24, 1950.

Numerous powdered-coal gasification processes have been proposed in which oxygen is used, and some are at present under development. In most of these, the design is such that difficulties with agglomeration probably will be minimized or eliminated, with the possible exception of those proposing the use of oxygen in a fluid bed. Certainly, it is anticipated that when the suspension gasification of powdered fuel is achieved on a commercial basis, it will be substantially independent of limitations on the nature of the fuel to be used. A comparable process using air would not, of course, be feasible because of dilution of the synthesis gas with the nitrogen from the air.

In a period when the supply of high-grade coking coals is known to be limited and when the investment cost required for large coke-oven installations is considered, a synthetic liquid fuels industry of any magnitude founded on the necessity for coke for gasification operations would not be realistic.

4. Greater adaptability to pressure operation

In either of the synthetic fuel processes discussed above, the synthesis gas or hydrogen must ultimately be available at an elevated pressure. This is 250 to 450 pounds per square inch for the Fischer-Tropsch and at least several times this for the coal hydrogenation.

In a gasification process using oxygen, the possibilities of conducting the operation at elevated pressures are attractive. As the volume of synthesis gas is three to five times that of the oxygen required, the compression costs for the over-all process can be reduced materially by compressing the oxygen only and saving the entire load of compressing the synthesis gas. Most of the oxygen-gasification processes can be adapted to pressure operation with some real advantages in the matter of equipment capacity and efficiency as well as of saving of synthesis-gas compression costs.

In an air-blown process such as the blue-gas set, the use of pressure operation probably would result in no advantage, as all of the air for combustion would have to be compressed, and this would amount to appreciably more than the volume of the synthesis gas produced. Theoretically, it would be possible to expand the products of combustion through gas turbines to recover the energy content, but this would entail such an increase in plant investment as to make it highly unattractive.

In those processes that depend on application of external heat to the gasification zones, the problem of materials of construction suitable for operation at the temperatures involved and at elevated pressures would be tremendous.

5. Higher range of attainable temperatures.

Another possible advantage of the use of oxygen is the fact that higher temperatures are attainable, which may be desirable in order to destroy the tars and oils from coal or to permit operation under slagging conditions.

At the present writing it is impossible to evaluate, in terms of dollars and cents, the various advantages of oxygen gasification given above. It is believed, however, that these advantages are real and demonstrable and will inevitably make development of a feasible synthetic fuels industry dependent upon efficient gasification of solid fuels with oxygen.

RELATION OF OXYGEN COST TO SYNTHETIC FUEL COST

In the absence of any commercial production in the United States of synthetic fuels by Fischer-Tropsch or coal hydrogenation, it is impossible to give cost figures from actual practice or to state precisely the relationship between costs of oxygen and synthetic fuels. However, enough information is available to make it possible to estimate these costs and to show how much the price of a barrel of synthetic fuel should change with a given change in the price of oxygen.

For the Fischer-Tropsch, for example, it is quite well established that there will be necessary about 690 pounds of oxygen to make 1 barrel of synthetic liquid fuel. This amount of oxygen at $5 per ton would amount to $1.72 per barrel, and at $3 per ton it would amount to $1.03. On this basis, then, each change of $1 per ton in oxygen will change the per-barrel cost of synthetic fuel from this process by about 35¢. For comparison, similar calculations made on coal would show that a change of $1 per ton in price would result in a change of about 40¢ per barrel.

In the coal-hydrogenation process, a relatively large part of the required hydrogen is to be recovered from the tail gases by low-temperature separation and produced by reforming the product methane with steam. For this reason, the oxygen requirement for coal gasification is only a fraction of that for the Fischer-Tropsch. It is estimated that about 90 pounds of oxygen will be required to make 1 barrel of synthetic fuel by coal hydrogenation. At $5 per ton, the oxygen cost would amount to about 22¢ per barrel of oil, and at $3 to about 14¢. On this basis, each change of $1 per ton in oxygen cost will change the per-barrel cost by about 4¢.

The foregoing was calculated on the basis of the maximum recovery of hydrogen from the tail-gas components and the use of coal gasification to generate the balance. Given oxygen at a low enough price, it may be economical to use the tail-gas components as plant fuel gas or to process them for sale as a general utility gas and to increase the proportion of hydrogen generated by coal gasification. This method of operation is discussed in a paper by F. L. Symonds, et al.[21] The selling price of the utility gas is expressed as a function of coal price and is such as to make this step probably desirable by the time a synthetic-fuel industry is competitive with petroleum. In that event, of course, the profit shown by the alternative operations would be credited toward the cost of the increased oxygen and coal required. At this time it is not felt that it is possible to predict where the division point would be on various commercial-scale operations.

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[21] Symonds, F. L., Laughrey, P. W., Skinner, L. C., Batchelder, H. R., and Donath, E. E., Public Utility Gas as a Byproduct of Synthetic Liquid Fuels Production: Proceedings of the American Gas Association, 1949.

The coal requirements for coal hydrogenation are almost the same as for Fischer-Tropsch, and changes in the coal price will have substantially the same effect on the cost of the product.

Cheap oxygen then is relatively more important for the Fischer-Tropsch than for coal hydrogenation, but in either case the cost of the oxygen necessary is an appreciable part of the cost of the final product, and variations in this cost may well affect sections of the final design.