chloride; absorption machines depend on the use of ammonia with water; but an objection to the latter process is the difficulty of dealing with the water which necessarily evaporates with ammonia. Carbon dioxide is not employed in naval work because the efficiency of the plant depends on a constant low temperature of the condenser water, and this efficiency is reduced in hot seas. Ammonia compression plants are also rejected by naval authorities since they usually leak; but ethyl chloride is employed, although there is danger of its vapour making an explosive mixture with air. Sulphur dioxide has largely gone out of use.

The present proposals depend upon the fact that solid ammonium nitrate absorbs ammonia to form one or more liquid compounds which evolve their ammonia when heated to 100° C. To prevent the formation of cellular layers which would retard the evolution of ammonia from the liquid, ammonium nitrate is mixed with kieselguhr in the ratio 3:2 by weight, and this enables the plant to be kept stationary. A 2-ton plant has been erected by the Seay Syndicate which produces 26 to 30 tons of ice per ton of coal. The container is made of aluminium sheeting, as iron is corroded by ammonium nitrate. With regard to the risk of fire when ethyl chloride is employed, it has been found by Henning that when methyl chloride is mixed with ethyl chloride in suitable proportion, the resulting liquid is not only non-inflammable but is itself a fire-extinguisher. Consequently cylinders of the liquid mixture stored on board ship may serve a double purpose.

ORIGIN OF THE PETROLEUM "CRACKING" PROCESS.*

W. M. BURTON.

The work done under my direction which has perhaps attracted the most attention was carried on principally in the laboratory and refinery of the Standard Oil Company at Whiting, Indiana, a suburb of Chicago, and consisted in devising ways and means for the practical conversion of high-boiling fractions of petroleum into low-boiling fractions in such a way as to ensure substantial yields of suitable products with a minimum loss and at a reasonable expense.

The problem became imperative with the advent of the internal-combustion engine about fifteen years ago. The most commonly-known example of such an engine is, of course, the automobile which, as constructed to-day, requires a fuel that evaporates at comparatively low temperatures, has a high heating value, burns without leaving objectionable residues, does not possess an objectionable odour, is low-priced, and can be produced in large quantities. Benzol, toluol, and alcohol are fairly well-suited for the purpose, but their cost and their small volume of production render them largely unavailable.

The low-boiling fractions of petroleum naturally came into use for this purpose, and up to about 1910 the supply of this fuel was sufficient to meet the demand. In fact, the automobile provided an outlet for the sale of these products, which, to some extent, had been a drag on the market in the oil world. The older refiners in the country will remember when these so-called naphtha products were thrown away and allowed to run down the

streams adjacent to the refineries, thereby causing a wilful waste and a fire menace to the surrounding neighbourhood.

Prior to 1910 the average yield of naphtha or gasoline products from crude oil in the United States was about 11 per cent., this yield representing only the amount of such products (of the quality desired at that time) normally present in the crude petroleum, their separation being secured by ordinary methods of distillation at atmospheric pressure; and, further, this small yield was sufficient to furnish all that was needed for gasoline stoves and other industrial purposes prior to the advent of the internal-combustion engine for transportation purposes.

When the automobile came into general use, however, it was perfectly clear that the normal yield of naphtha products suitable for fuel in self-propelled vehicles would not be nearly enough. At that time our refineries were selling about forty per cent. of the products of crude oil for use as fuel and for gas-making purposes in lieu of coal. The remaining sixty per cent. represented the normal yield of naphtha and gasoline, illuminating and lubricating oils.

The above-mentioned forty per cent. fuel and gas oil comprised fractions boiling between 225° C. and 375° C. These oils could, if necessary, be withdrawn from the market, and our problem was to convert them as far as possible into fractions boiling between 40° C. and 200° C., the product to be equal in quality to normal naphtha products and the yield and operating expense to be commercially practicable.

Our first experiments were directed towards making a suitable product by superheating the vapours of the high-boiling fractions, but without pressure, somewhat according to the practice observed in making "Pintsch" gas. We soon found, however, that this so-called "cracking" in the vapour phase required a temperature so high that the aliphatic hydrocarbons contained in the petroleum were largely converted into cyclic and aromatic bodies and fixed gases—unsuited for our purpose. The yield was poor and the quality most undesirable. Obviously our problem included the proposition of reducing the molecular weight without changing the general structure.

We next tried the use of various reagents and catalysers, such as aluminium chloride and ferric oxide. Anhydrous aluminium chloride, indeed, produced some rather remarkable results. The yield and quality of naphtha products were fairly satisfactory, but there was a substantial loss of oil in the operations and the first cost of the anhydrous aluminium chloride, as well as the difficulty in recovering it from the residues, rendered this plan unattractive.

Nearly thirty years ago Sir Boverton Redwood and Prof. (now Sir James) Dewar, in England, had patented a pressure-distilling process for the purpose of increasing the yield of kerosene oil from the residues of Russian crude petroleum, but it was never applied industrially. It had been known, therefore, for some years that distilling petroleum under pressure served to break down the high-boiling fractions into low-boiling fractions; but, as far as we could learn, no one had ever done it on the large scale, and, in fact, such a proposition could not commend itself to a practical refiner because of the obvious dangers from explosions and fires that would be present in handling large stills under such conditions.

But having tried everything else that suggested itself, we attacked the problem of distilling petroleum in considerable quantities (8000 to 12,000 gallons) under pressure of about five atmospheres. The first still we built was of a welded design and was planned to handle 100 gallons of the high-boil-

*Address delivered by the recipient of the Perkin Medal at the meeting of the American Section, January 13, 1922. (cf. p. 488 of this issue.)

ing fractions. Obviously, the raw material first to be tried consisted of the so-called fuel oil, or reduced crude, i.e., the residue of crude oil after the more valuable products had been removed. We soon found that we could not work profitably with this product; when distilled with or without pressure it produced quantities of cake that deposited on the bottom of the still and caused a red-hot bottom that would not stand any rise in pressure. The next proposition comprised the use of high-boiling distillates from the crude petroleum, viz., oils boiling at 225° C. and upwards. By using these oils as raw materials we secured our first encouraging results. We distilled these distillates under a pressure of about five atmospheres and were thereby able to keep down the temperature to a moderate figure, the cracking being done in the so-called liquid phase. By doing the work in this way we found to our intense gratification that the low-boiling fractions produced belonged mostly to the aliphatic or paraffin series, which were easily deodorised and finished into products suitable for sale. Further, the yield of saleable liquid was good and the production of fixed gases and coke was small.

Experimentally, therefore, our work was successful. But the big problem remained to be solved. Could we build large equipment that would, in a practical way, secure the desired results and at the same time be durable and reasonably free from the fire hazard that always attends operations in an oil refinery? Some of our practical men said we could, but more of them said we could not. In this case, however, the majority was overruled, and we immediately prepared plans and specifications for a still 8 ft. in diameter and 20 ft. long, built of 0.5-in. mild steel plate, which would hold 6000 gallons of raw material. It had a safety factor of 5, the working pressure being 100 lb. and the bursting pressure 500 lb.

The still was built and charged, with many misgivings on the part of the doubters, but with boldness and confidence exhibited by the rest of us. So soon as we had the still hot and pressure began to develop we encountered our first difficulty. The still was built in a workmanlike manner, and would have made a good steam boiler, but we found that rivets and seams which would not leak under steam pressure leaked badly under oil pressure. It was difficult to induce boilermakers to caulk the leaks while the still was hot and under pressure, but we found men bold enough to do it, and the first run was sufficiently encouraging to induce us to proceed further. But the leaks persisted until Nature came to our aid; the minute portions of oil in the leaks gradually carbonised, and the leaks closed without our aid.

The experiments with the large still confirmed our results with the small one, viz., the yield of suitable gasoline fractions was good; the loss was trifling; the cost was reasonable; and with close caution and supervision the fire hazard was not excessive. Further, we were astonished to find that the residue remaining in the still contained substantial quantities of asphaltine actually created (from a distillate containing none of it) by distillation under pressure.

We learned early in the work that operating at moderate pressure required a substantial dephlegmating system that would return to the still fractions boiling too high for our purpose, and allow the others to pass on.

A suitable safety-valve that would operate properly with oil vapours at high temperatures had to be devised. After making a number of runs with our 8×20 ft. still, and in view of the fact that the demand for gasoline was increasing at a rapid rate, we asked for an appropriation of one million dollars to build sixty pressure-stills 8 ft. in diameter and 30 ft. long, each holding 8000 gallons of raw

material. It required considerable argument to convince any of our directors that such a revolutionary proposition could possibly be successful, but finally they voted in favour of it, and we went ahead.

It would require much time to give a full account of the minor difficulties that arose. We had solved the big points, but there were many smaller ones. For successful results we must operate with the oil at temperatures from 370° to 400° C. in the still. At 450° C. steel begins to lose its tensile strength and its capacity to withstand pressure. It is clear, therefore, that with this narrow margin great caution must be exercised to prevent overheating. The human element enters here, as it does in every feature of pressure-still operation, but we operated over eight years with hundreds of these stills in daily use and manufactured millions of barrels of gasoline by this method before we had a fatal accident.

From the humble beginning of the 100-gallon still in our experimental laboratory, the Standard Oil Company of Indiana has in operation to-day over 800 pressure-stills with a gross charging capacity of 8 million galls., and licensees under our patents are operating as many more, giving a daily production of 2 million galls. of gasoline out of about 12.5 million galls. total daily output in the United States and Canada.

This amount of gasoline makes possible the use of two millions of motor vehicles more than could otherwise have been supplied from a given consumption of crude petroleum, and as a corollary of that proposition, and assuming 20 per cent. of gasoline as a normal average yield from crude oil, the pressure-still process is conserving for future consumption an amount of crude oil nearly equal to 100 million barrels per year.

The consumption of gasoline by internal-combustion engines during the past decade has increased at a terrific rate. In 1910 the United States consumed approximately 700 million galls., and for 1920 the Bureau of Mines statistics show a total gasoline production of four billion six hundred million galls., of which 850 millions was made from natural gas, over three billion galls. made by straight crude-oil distillation, and 750 million galls. made by the "cracking" process. Further, statistics show that whereas the increase in crude-oil production during the past decade has been 142 per cent., the increase in gasoline production has been over 700 per cent.; and although some of this gasoline has been exported, the larger portion has been consumed by the ever-increasing number of automotive vehicles in this country.

The increase in production of crude oil has not been commensurate with the increased demand for its products, but the pressure-still process has, at least, filled part of the gap. Naturally, one is inclined to speculate on the adequacy of future supplies of these important commodities. One suggestion would be that some of the large amounts of oil now being used for fuel and gas-making purposes be replaced with coal, and substantial portions of the oil used for making gasoline, the coal consumption, in turn, to be replaced in part by the further development of hydro-electric power.

The American people are notoriously wasteful in the use of natural resources, with which they are so richly endowed. It is hoped that the work outlined above will be considered a slight contribution towards the curtailment of such waste.

It would be obviously unfair and unjust to close this paper without duly acknowledging the work done by my associates in successfully establishing the pressure-still process. Our patent attorneys, represented by Mr. Russell Wiles, contributed many useful and practical suggestions, and if it had not been for the invaluable assistance of Dr. R. E.

Humphries, Mr. E. M. Clark, and Mr. T. S. Cooke, and many others connected with the Standard Oil Company, of Indiana, satisfactory results would never have been secured.

STANDARDISATION OF JACKETED PANS.

The Sub-Committee appointed by the Joint Research Committee of the Association of British Chemical Manufacturers and the British Chemical Plant Manufacturers' Association to consider the standardisation of steam-jacketed pans, has devoted, in the first place, its attention to cast-iron pans, as these are in the most urgent need of standardisation. With the object of designing a standard pan of maximum efficiency in respect of heating surface, working capacity, and strength, a series of drawings showing various shapes and flanges was sent to chemical manufacturers; a précis of the replies was forwarded to the plant makers, and their approval of the settled designs solicited.

As a result of the inquiry it was agreed that the standard working capacity (i.e., the heating capacity) for the types of cast-iron and enamelled cast-iron pans selected should be calculated from the underside of the bolting-flange of the liner. The actual capacity is greater, e.g., the deep pan of 25 gallons has an actual capacity of 34 gallons; so that in future a manufacturer will know that he can work 25 gallons in a standard 25-gallon pan, and not about 18 gallons as hitherto.

After very careful examination the Committee has decided to adopt a two-radii pan. The metal being cast-iron, it was found impossible to stipulate one thickness; to surmount this difficulty, and also to allow for a higher working pressure, the Sub-Committee has laid down limits of thickness. For a working pressure of 35 lb. the thickness of the metal must be within the limits stated, but for a 40-lb. or 45-lb. working pressure the thickness must be the outside limit stated on the drawings.

The Committee has also considered the possibility of fitting wrought-metal linings to the jackets, but has come reluctantly to the conclusion that it would be impossible to design cast-iron jackets for all the sizes considered that could be fitted with such linings. It is suggested, however, that in the deep patterns up to and including the 100-gallon pan, the wrought-metal liner could replace that of cast iron. The cast-iron liners have been designed for enamelling, and the Committee draws attention to the thickening of the metal at the flanges. This is considered to be important, and calculations have been made to allow sufficient metal so as to ensure gradual radiation at the non-heated contact points. The edges have been rounded so that the inside edge can be well covered with enamel, which will then not flake off when a stirrer is used. The lugs for the feet have all been cast on to the jacket with a strengthening web, and the inlets and outlets have been made to conform with the sizes of the pans. It will be noticed that the water drain is in the centre of the bottom of the jacket and not at the side as hitherto; it is generally agreed that the latter practice is wrong. The steam distributor, which is not shown in the drawings, is best inserted at the bottom, where the steam space is greatest and where there is less risk of the liner expanding unevenly. Bosses are cast on the upper edge of the jacket for safety-valve and air blow-off. Should a chemical manufacturer desire the steam-inlet on the top, which in the opinion of the Committee is wrong, a baffle-plate must be inserted. These steam distributors or baffles have not been considered, as the Committee is of opinion that they do not require standardising. In every case the steam

space has been carefully calculated and graduated for a steam-inlet at the bottom of the pan, so that steam entering the jacket shall cause the rise of temperature to be as even as possible.

The Sub-Committee desires to draw special attention to the 75- and 100-gallon shallow pans. It has been ascertained that cast-iron and enamelled-iron are not always used for these large sizes, particularly for the 75-gallon size, and the Committee has therefore designed the 75-gallon lining to fit into the 100-gallon jacket, making only one jacket necessary for these two sizes. In this way it is hoped to dispense with the standardisation of another unit. Attention is also drawn to the fact that the 50-gallon shallow pan and the 100-, 150- and 200-gallon deep pans have all the same diameter of flange on the liner, so that the universal cover, which the Committee is now designing, will fit them all.

The Committee has also taken into consideration the fact that this deep type of pan would make an admirable still, and the Sub-Committee is to discuss the question of providing these pans with outlets so that they can be converted immediately into stills, or stills into pans, using the one standard cover.

The designs given in the report represent the results of the examination of a very large number; each one of them has been carefully investigated, calculations of strength have been considered, and, in the opinion of the Committee, the specifications proposed will ensure plant of maximum efficiency.

The Sub-Committee suggests the adoption of the following tests, and that a certificate embodying the results be issued with every pan:—

Cast-iron Steam-jacketed Pans.

A. For a working pressure of 35 lb. per square inch (shape as in drawings):—Thickness of metal to be within the limit stated on the drawings; hydraulic test, 75 lb. per sq. in.; steam test at working pressure for at least half-an-hour.

B. For working pressure of 40–45 lb. (shape as in drawings):—Thickness of metal to be the greater thickness stated on drawings; hydraulic test, 90 lb. per sq. in.; steam test, 45 lb. per sq. in. for half-an-hour.

Enamelled Cast-iron Standard Steam-jacketed Pans.

Tests as above, with the exception of the steam test, which is to be applied as follows:—The pan to be filled to limit capacity with cold water, steam to be applied to the jacket at the working pressure, and the contents boiled. After boiling from 5 to 10 minutes the water to be removed and the steam to be kept applied for at least 15 minutes to show up pinholes, flaking or crazing.

The above is the substance of the introduction to the report, which also contains a table of specified dimensions and nine drawings of the following sizes of enamelled, cast-iron, standard steam-jacketed pans:—

Working capacity, gallons.						Actual capacity, gallons.
10	..	..	..	..	..	15
25	..	..	..	..	..	34
50	..	..	..	..	..	63
100	..	..	..	..	..	128
150	..	..	..	..	..	180
200	..	..	..	..	..	233
SHALLOW TYPE.						
25	..	..	..	..	..	43
50	..	..	..	..	..	73
75	..	..	..	..	..	112
100	..	..	..	..	..	130

The table of dimensions and three drawings are reproduced on the following pages. The full report may be obtained from the British Chemical Plant Manufacturers' Association, at 160, Piccadilly, London, W. 1, price 2s. 6d.