

MOLASSES STILLAGE

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Concentrated stillage can be carbonized in a stationary retort in acid or alkaline condition. Low-temperature carbonization not exceeding 700° F. yields a hard, brittle, nonhygroscopic product. The stillage treated with alkali metal compound at 8.5-9 pH yields the softest carbonized product; an acid stillage of 4-4.5 pH is the hardest. Lime has a tendency to give the densest product; stillage treated with alkaline metal compound gives the most porous, while the density of the acid char lies between the other two. Continuous feeding of the concentrated stillage to the retorts results in the densest product. Up to 650° F. the loss of organic nitrogen is very low. The separation of potassium sulfate from ammonium chloride by means of dilute alcohol is very sharp. Low-temperature carbon is suitable for chicken feed purposes or as a substitute for wood charcoal.

DISTILLERIES processing molasses are frequently confronted with the problem of disposing of stillage. From an engineering standpoint the conversion of stillage to a marketable form has been solved, but from an economical standpoint much remains to be done. Values recoverable from the stillage depend upon the quality of raw material processed. It may be blackstrap molasses from Cuba, Puerto Rico, or the Hawaiian Islands, or so-called high-test molasses. Analyses are given in Table I.

The value of the stillage depends upon its organic matter, which is mostly nonsugars, and inorganic compounds such as potash (K_2O) combined with chloride, sulfate, and organic compounds. For the recovery of these organic nonsugars, the usual procedure is spray or drum drying of the concentrated stillage. If the yeast has not been extracted, the stillage will contain vitamins such as riboflavin, niacin, and pantothenic acid. The latter is also present in cane molasses, and according to Jukes (3), Cuban molasses sometimes has as little as 5 micrograms of that compound per gram. Hawaiian has 70 to 100, while Louisiana has 70 to 80 micrograms.

The first step in recovering values from the stillage consists of concentrating it in multiple-effect evaporators. It has been found that acid stillage with a hydrogen-ion concentration of 4-4.5 cannot be concentrated economically above 33-35° Bé., while alkali stillage may be evaporated to 42-44° Bé.

A process for the low-temperature carbonization of concentrated molasses stillage is described here. Patents have been granted (6) on some phases of this work, while another is the subject of a recent patent application. Attention should be called to the fact that the process is not universally applicable. Special local conditions would warrant the use of the process in one form or another, while in other localities it would be uneconomical. Therefore this process should be considered with the above facts in mind.

It has been found that stillage can be carbonized at such a low temperature that most of the organic nonsugars are carbonized practically without loss of nitrogen, and also that the final product is nonhygroscopic and can be handled easily. The aim was to produce a material which could be lixiviated easily and the water-soluble potash compounds separated from the char. A further aim was to convert potassium chloride into sulfate, as the latter is preferable for fertilizer purposes.

EXPERIMENTAL UNIT

While continuous carbonization would appear to be desirable and is being used by the author, for specific reasons a stationary retort appeared preferable. For experimental purposes a retort was made of $1/2$ -inch common steel, 1.5 feet wide, 6 feet high, and 8 feet long. It was tapered toward the top and mounted in a

firebrick setting heated by two oil burners. No provision was made for agitation, and heating was indirect. The retort setting was such that all the stillage was within the heated area of the retort. Figure 1 shows the complete experimental unit provided with the usual temperature and draft recorders, with a meter for measuring the quantities of fuel oil used. The size of the retort was sufficient for the handling of 150 gallons of concentrated stillage yielding 620 pounds of char and potash. Attention must again be called to the fact that, although the volume of acid and alkaline stillage was the same, owing to the latter's higher density, more finished product could be obtained from it.

The composition of the organic compounds in the stillage is not uniform, especially if the raw materials come from different localities. Therefore, the yields of carbonized product will vary. However, it has been found that, if the carbonization has been carried out at a temperature not exceeding 650° F., the product will contain practically all of the original nitrogen. The structure of the carbonized product varies, not only on account of the variation in the composition of the organic nonsugars but also on whether it was acid or alkaline, whether it contained lime or was heated rapidly or slowly, and whether the charge was carbonized while the stillage was fed continuously or intermittently to the retort. The final product had the following structural characteristics:

1. Greater density resulted from acid stillage than from alkaline.
2. The presence of lime sometimes yielded a product as solid and hard as a rock.
3. Heating a full charge of stillage resulted in a more porous carbonized product than intermittent feeding.
4. Lixiviation of the carbonized product containing lime was incomplete; the alkaline char was the best.
5. Acid stillage yielded a potash char of greater crushing strength than alkali-treated stillage.
6. An excess of alkali in the stillage, with a pH of over 9, resulted in a finished product which could be powdered merely by pressing it between the hands.

COMMERCIAL UNIT

With the best conditions determined for an experimental retort for low-temperature carbonization of the molasses stillage, larger retorts for the commercial carbonization of stillage were built. To obtain a uniform and constant temperature throughout the retorts, they were heated by radiated and conducted heat. Radiated heat was supplied by the brick wall forming the compartment in which the retort was set, and provision was made for a suitable circulation of hot gases around the retort.

Figure 2 shows the position of the retort. It lies in a heating chamber separated by a wall from the combustion chamber.



Figure 1. Experimental Furnace for Low-Temperature Carbonization of Molasses Stillage

These walls radiate heat upon the retort. Portholes are provided in these walls which, in combination with the proper flues, enable the production and control of the desired gas circulation as shown in Figure 3. The gas circulation affords the principal control of the temperature in the retort, and this circulation is regulated mainly by the number, size, and position of the portholes, and in part by dampened flues. These factors vary, therefore, with changes in the size and shape of the retort and with variations in the maximum temperature desired.

Because of the forward flaring shape of the retort, provision has to be made to supply more hot gases around the forward portion of the retort. This is accomplished by the arrangement of the portholes, and experience showed that in general the total area of the flue openings should be at least twice the total area of the portholes per partition wall.

Further details of the retorts are shown in Figure 4, where the individual flue gases in the back of the furnace are led into a main header. Flue outlets in the front are not shown. The setting arrangements are pictured in Figure 5 and the retorts in Figure 6. As the concentrated acid stillage had a pH of 4 to 4.5 and the alkali stillage of 8 to 8.5, and since the carbonization temperature was below 700° F., common cast iron retorts were used. Each retort consists of three sections. The over-all dimensions of the retorts are 5 feet high and 15 feet long. The width varies since

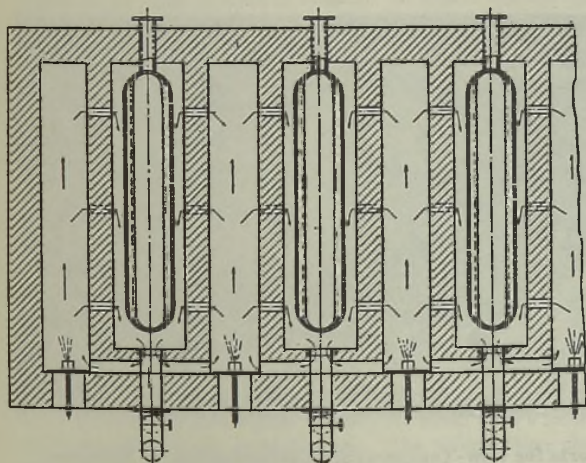


Figure 2. Transverse Sectional Elevation of Retorts

the retort is tapered; it is 18 inches wide in front and 12 inches in back, and is closed. The front is provided with a door, supported on hinges so that at the end of the run the full charge can be pulled out. The retorts are somewhat similar to Koppers coke ovens.

During carbonization the stillage has a tendency to foam, and this foaming again depends upon the quality of the molasses fermented and whether it was treated with an alkali metal compound or not. Other factors which must be considered during low-temperature carbonization are the change in the consistency of the product. No matter what temperature is employed or how rapidly the heat is applied, the stillage foams a great deal, shrinks after foaming, and then goes through a plastic stage before it becomes solid and carbonized.

The potash char can be removed from the retorts in large lumps which, after standing for some time in air, break up into sizes of 3 to 8 inches. The yield of this char is 4.5 pounds per gallon of concentrated stillage of 33° Bé. It required approximately 41 hours per charge and, by producing 129,260 pounds of potash char, the yield per charge averaged 1235 pounds. The carbonized stillage char contained:

Total nitrogen	1.87%
Water-insoluble nitrogen	1.69
Water-soluble nitrogen	0.18
Total potash (K ₂ O)	15.44
Water-soluble potash (K ₂ O)	15.10
Carbon	32.57

Calculating the yields on a unit basis: 1 ton of molasses (168 gallons) yields 730 gallons of beer, 84 gallons of concentrated stillage, and 378 pounds of potash char.

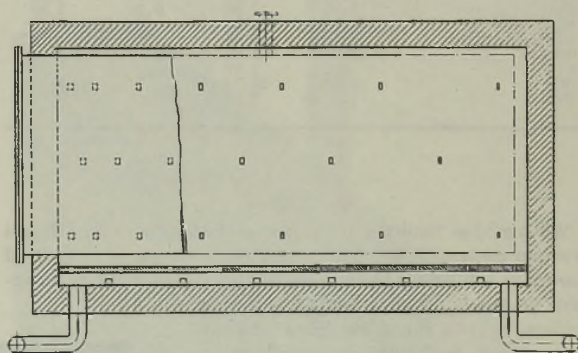


Figure 3. Longitudinal Sectional Elevation of Heating Chamber

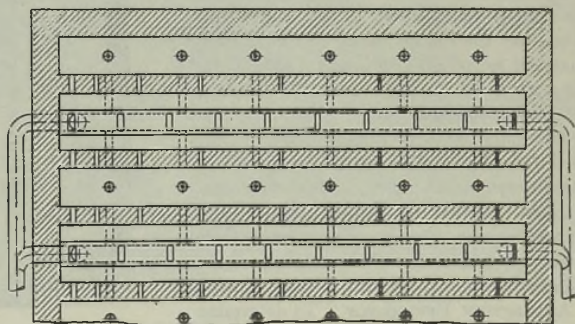


Figure 4. Sectional View of Flue Outlets

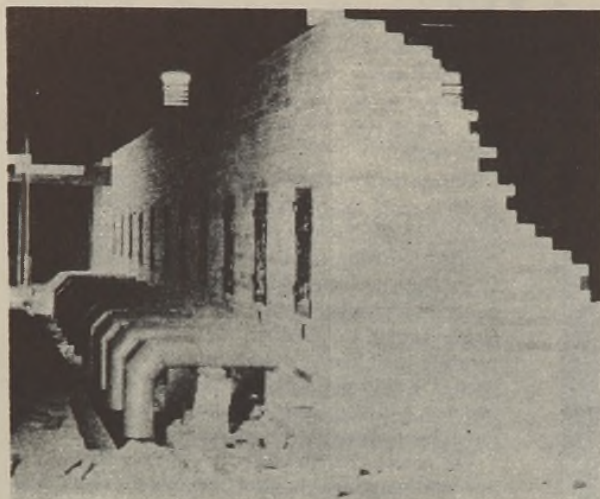


Figure 5. Flue Arrangement

Coconut char was found best, then stillage, wood charcoal, and bone char.

CARBON CONTENT. The various chars analyzed as follows (5):

	Coconut	Wood	Bone	Stillage
Moisture				4.64
Volatile matter + fixed C	97.86	97.76	9.30	94.25
Ash	2.14	2.24	90.70	5.75

DISCOLORATION. The milling companies desire charcoal which will not discolor the feed. Although the method of testing the charcoals is crude, it appears to be satisfactory since some mills are using it regularly. Ten grams of the carbon are placed in a tin can, 4 inches in diameter and 3 inches high, which contains six ball bearings weighing 90 grams. The can is provided with a tight cover and moves rapidly two hundred times in a swirling motion. The crushed charcoal is screened through a 100- and 200-mesh screen, and the fines are mixed with chicken feed and rolled in a ball mill. The degree of coloration of the stillage feed with the various charcoals are as follows: coconut charcoal best, followed by molasses stillage char, bone char, and wood char.

CRUSHING STRENGTH. The method of Knowles (4) for crushing carbons has given satisfactory results. The results of screening the chars up to 50, 100, 200, or above 200 mesh are:

Mesh	Coconut	Wood	Bone	Stillage
Up to 50	91%	55%	65%	73%
50 to 100	4	10	17	11
100 to 200	2	10	8	9
Above 200		25	10	7

These results show that the stillage char has a greater crushing strength than wood and bone char.

BY-PRODUCTS

During the low-temperature carbonization not only gas and tarry matter are driven off, but also large quantities of water. As the concentrated stillage had a density of 33–44° Bé., the water content of the tars was 50–75%. The vapors leaving the retorts around 500° F. pass through a standpipe of conventional design. A blower forces them through a water scrubber which reduces the vapor temperature and precipitates most of the tar and light oils which are collected in a tank as shown in Figure 7.

CONVERSION OF POTASSIUM CHLORIDE TO SULFATE

The potash (K_2O) in the molasses is present as sulfate (25–30%) and chloride (25–40%), and is combined with the organic nonsugars in the amount of 25–40%. If the recovery of the car-

TABLE I. COMPOSITION OF RAW MATERIALS USED IN MANUFACTURE OF MOLASSES ALCOHOL

	Cuba	Hawaii	High Test	Beet (Mich.)
°Brix	82.70	86.10	84.30	86.80
°Baumé	43.77	44.91	44.53	45.24
Sp. gr., 20/20° C.	1.4328	1.4492	1.4437	1.455
Sucrose, %	35.53	27.89	16.93	48.43
Invert sugar, %	15.77	15.55	58.33	
Raffinose				1.28
Total sugars, %	51.30	43.44	75.26	49.71
Nonsugars, %	31.40	42.66	9.04	37.09
Ash, %	9.50	12.91	1.93	10.95
Water, %	17.30	13.90	15.70	13.20
Ash composition, %				
K_2O	45.91	25.55	49.20	57.01
Na_2O		2.60		7.26
CaO	16.12	19.08	0.10	1.69
MgO		11.35		0.59
$Fe_2O_3 + Al_2O_3$	1.53	0.45		
SiO_2	3.78	3.08		
Cl		1.27		2.78
SO_3	15.05	20.70		8.95
P_2O_5		2.05		3.08

CHAR

When sold as fertilizer, the char is evaluated by its potash and nitrogen contents; the high percentage of carbon is considered merely as a filler. Therefore experiments were made to determine the possibility of using this carbon in poultry feed as a substitute for wood charcoal, as well as for the production of activated carbon.

The first step in the recovery of the low-temperature carbon consisted of leaching the finely or coarsely ground char (8). When dry the leached char, free of potash, analyzed as follows: moisture 4.64%, volatile matter 47.85, fixed carbon 41.80, ash 5.71 (total 100%).

The main requirements for a char to be used for poultry feed purposes are: high gas adsorption efficiency, high carbon content, no tendency to discolor the feed, and high crushing strength. Experiments were made to ascertain these qualities in the stillage char and the results are as follows:

ADSORPTION EFFICIENCY. To determine its efficiency, comparisons were made with other carbons by using carbon dioxide gas.

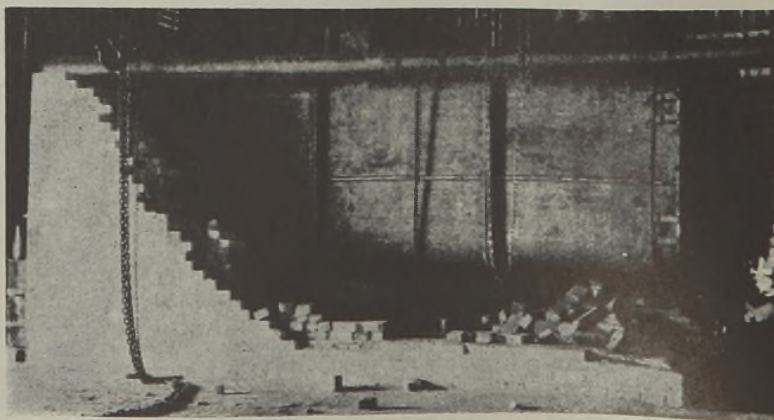
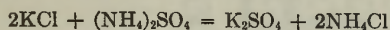


Figure 6. Retorts for Low-Temperature Carbonization of Molasses Stillage

bon is contemplated, the potash must be removed by lixiviation (7). During low-temperature carbonization some of the potash is converted into carbonate, and the lixiviated potash may be similar to the ash obtained by incinerating the stillage.

In some localities the potash is not desired as chloride and carbonate; in fact the latter, being alkaline, has a detrimental influence upon crops and fruit trees. Therefore the problem was to find a process whereby all the potash could be converted into sulfate without expensive chemicals and equipment. At first it appeared necessary merely to treat the potassium chloride, carbonate, or potash, combined with organic matter, with sulfuric acid, thereby liberating hydrochloric acid (1) and converting the potash salts to sulfate. However, the difficulties encountered in disposing of such large quantities of hydrochloric acid and the purchase of sulfuric acid for an inexpensive chemical such as potassium sulfate made this procedure appear prohibitive. Other possibilities suggested were the treatment of the potash salts with ammonium sulfate. A similar process with sodium chloride was described by Hochberger (2).

It appeared more economical to convert the potash salts to sulfate by treating with ammonium sulfate, according to the equation:



The ammonium sulfate, as purchased, is sold on its nitrogen content; therefore the sulfate ion to be used in this process could be obtained free. Another apparent advantage was that the ammonium chloride could be marketed much more easily than hydrochloric acid.

According to Seidell (7) potassium sulfate is less soluble in cold water than ammonium chloride. Therefore it appeared that their separation would not offer a serious problem. However, it was found that in low-temperature carbonization not all organic compounds are carbonized, and upon treatment with water these uncarbonized materials dissolve, impart a coffee-like color, and prevent a smooth separation of potassium sulfate from ammonium chloride. If present in small quantities, these organic compounds have a tendency to increase the fluxing properties of the ammonium chloride during the galvanizing operation, and some firms prefer it to the white ammonium chloride crystals.

SEPARATION WITH DILUTE ETHANOL

Experiments with ethanol showed that the separation of potassium sulfate and ammonium chloride is very sharp and that products of high purity are obtainable. The solubilities of potassium sulfate in ethanol of specific gravity 0.939 at 140° F. is 0.92 part in 100 parts of solvent; 30.1 parts of ammonium chloride are soluble in the same amount of solvent. At first it appears that the cost of denatured ethanol is prohibitive. Obviously prewar prices are to be considered. Alcohol recovery plants are usually operated at such high efficiency that the loss of solvent is not very great, especially when it has an alcohol content of 45–55% by volume.

The process for the double decomposition is as follows: After the low-temperature potash char is crushed to 20-mesh size, it is lixiviated on the countercurrent principle for the separation of carbon and potash salts. To the potash liquor at a specific gravity of 1.15–1.2 is added ammonium sulfate, preferably in saturated solution, exceeding somewhat the stoichiometric quantity required. The reaction is rapid, and 30–35% of the potassium sulfate is precipitated in 99.5% pure form. The first crop of potassium sulfate is separated by centrifuging, and the mother liquor is concentrated until a specific gravity of 1.25–1.35 at 180° F. is attained. The specific gravities depend upon the water-soluble organic compounds which have a retarding influence upon the crystallization. The reverse takes place in the manufacture of sugar where the inorganic salts, having so-

called mellisogenic properties, retard the crystallization of sugar and thus result in the formation of molasses.

When the proper specific gravity has been attained, the solution is cooled with water and agitated; this treatment precipitates most of the potassium sulfate and ammonium chloride. The crystals also contain some water-soluble organic matter and low-temperature tar and oils. Most of the latter is found in the mother liquor with the excess of ammonium sulfate, some potassium and sodium sulfates, and ammonium chloride. The mother liquor at proper concentration is returned to the retorts.

The dark precipitate of potassium sulfate and ammonium chloride, freed from the mother liquor, is treated with denatured ethanol having a specific gravity of 0.92–0.94 at 140° F. The great differences in the solubilities of these salts in the solvent permit quick and easy separation. Potassium sulfate of 99% purity remains undissolved, while the ammonium chloride in solution is recovered by crystallization after the removal of the alcohol. The ammonium chloride thus obtained has a purity of 99.5%, and the mother liquor from these crystals, high in organic impurities, is returned to the liquor for char leaching purposes.

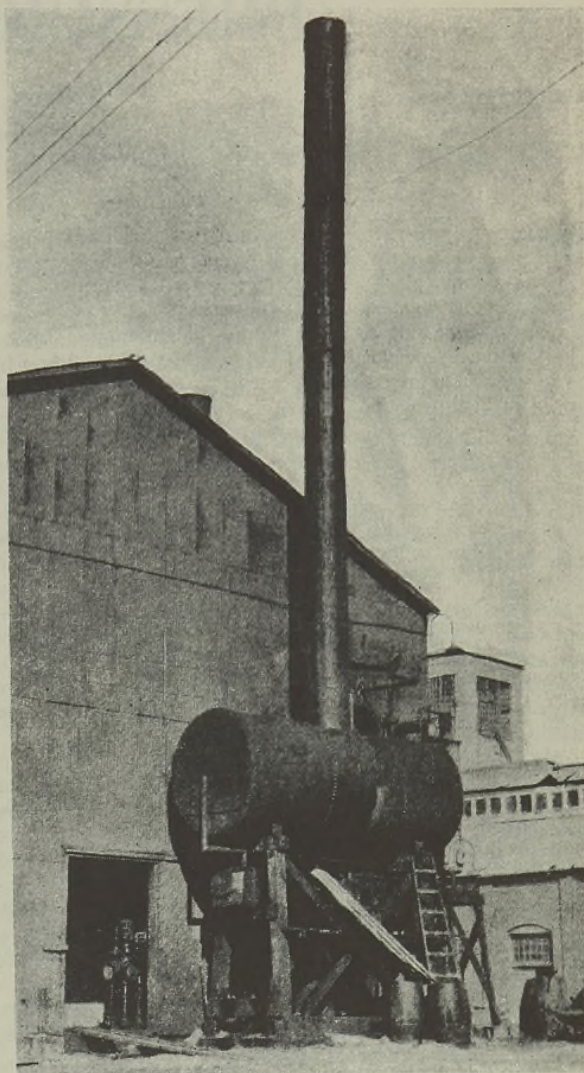


Figure 7. Scrubber for Tar and Vapors from Low-Temperature Retorts

The process described above uses ammonium sulfate. Instead of this salt, ammonium nitrate can be employed. The concentration of the liquor in this case will be 1.3-1.45 at 180° F.

POSTWAR OUTLOOK

The availability of large domestic and foreign supplies of potash salts after the war would not warrant the recovery of the potash and char by concentrating and carbonizing the molasses stillage at a low temperature unless some local or operating condition, especially in the West Indian or other sugar producing countries, offered favorable circumstances. Since the organic non-sugars are of vegetable origin, they yield products similar to those obtained by the low-temperature carbonization of wood. Therefore, the char has possibilities of being used in chicken feed or for other purposes similar to those for which wood charcoal is utilized.

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HIGH SPEED AGITATOR FOR PRESSURE VESSELS

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THE use of pressure equipment in research laboratories has increased steadily over the last several decades to the point of being commonplace. Many investigators have found it possible, through temperature or mass action effects, to increase greatly a reaction velocity or to shift an equilibrium in a desirable direction by conducting the reaction under pressure. In those cases where the reactants occur in a single phase, such as gaseous or liquid solutions, stationary apparatus is often satisfactory. However, if two or even three phases are involved, the rate of reaction can be further increased by providing some means of agitation. At the same time heat transfer between the stirred mass and the vessel wall is materially increased. Numerous devices to mix or stir the contents of a pressure vessel have been reported in the literature. Phillips (12) and Groggins and Hellback (7) described an arrangement whereby cylindrical bombs are rotated in a constant temperature bath. Other designs which depend on either rotation of the reactor itself or of internal blades for agitation are described by Tongue (13), Laupichler (9), and Fischer (5). Several authors (1, 4, 11) have described a shaking or rocking autoclave of a type which has been commercially available for a number of years.

Mechanical difficulties—such as bleeding gases in and/or out of a vessel, attaching gages, condensers, heat exchangers, or safety disks, maintaining constant pressure, etc.—which are encountered with rotating, shaking, or rocking autoclaves can be greatly reduced by an externally powered and internally stirred autoclave (9, 13). However, this type of equipment is not entirely without fault. If the vessel is to be used at pressures in excess of several thousand pounds, it is difficult to obtain a stuffing box which will remain gastight for any considerable length of time; and while gas leakage can be reduced by a lantern-lubricated gland, contamination of the reaction mixture with the lubricant then becomes a problem. Power losses, through a packing gland, result in a high initial and operating cost and tend to reduce the rotation speed of the stirrer so that, from the standpoint of agitation and cost, the value of this type of autoclave is often questionable. A 750-cc. autoclave built in

the Coal Research Laboratory for service at a pressure of 3000 to 6000 pounds per square inch required 1/4 horsepower to turn a stirrer at 120 revolutions per minute. Tongue (13) described several small laboratory autoclaves of the same type which had similar power requirements. These faults exceed reasonable limits as the size of the autoclave is reduced, since amount of leakage, size of power installation, and amount of agitation will remain fairly constant with wide variation in the volume of the pressure vessel.

A more nearly ideal reactor would be one in which the stirring mechanism and reactants are contained within the same wall. Calvert (3) in 1914 obtained a patent on this basic idea which covered not only motor-driven stirrers, but also circulating pumps. MacMillan and Krase (10) and Holloway (8) published a detailed description of an autoclave in which the stirrer and motor operate under the same gas pressure. Recently (6) a method of obtaining agitation by means of a magnetically operated plunger was reported.

This paper describes a totally enclosed motor and agitator, built to operate under more severe conditions with respect to pressure, temperature, and chemical attack than those mentioned above. The stirrer assembly (Figure 1) is constructed as an integral unit which is attached to the bomb head by means of the threaded lower end. The autoclave, shown dismantled as well as assembled to run in Figure 2, was built in these laboratories several years ago to study the hydrogenation of coal in aqueous alkali at temperatures and pressures up to 400° C. (750° F.) and 6000 pounds per square inch. Violent agitation is required in this reaction to produce not only the maximum possible gas-liquid interface, but to prevent the coal particles from fusing together. Sufficient turbulence was obtained in this autoclave by rotating a 2-inch nickel propeller at 1500 r.p.m. in a 750-cc. nickel-lined cylindrical bomb of 3-inch internal diameter.

The body and top closure for the assembly were machined from chrome-vanadium steel (SAE-6145) forgings which were heat-treated and drawn at 900° F. in a salt bath after all machine work had been finished. Data available for this alloy indicate