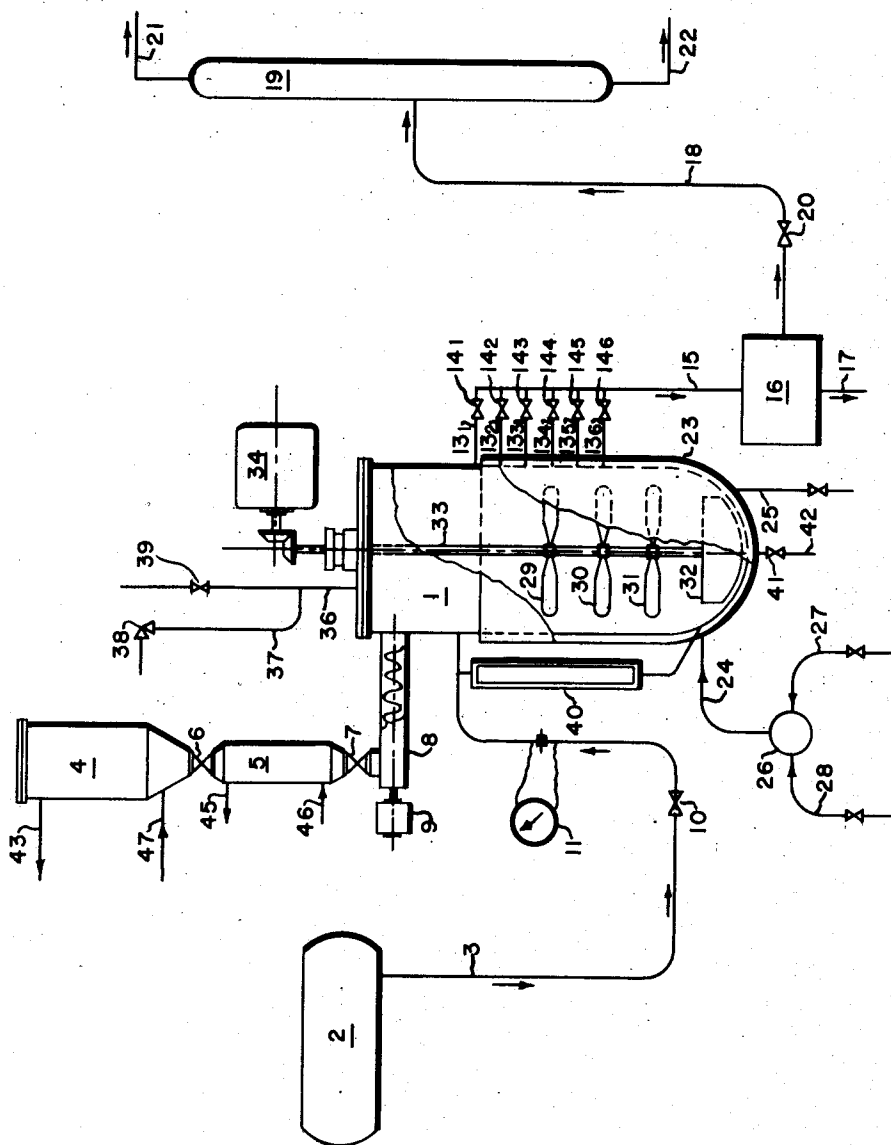


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MANUFACTURE OF TETRAETHYLLEAD

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MANUFACTURE OF TETRAETHYLLEAD

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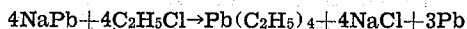
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6 Claims. (Cl. 260—437)

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This invention relates to the manufacture of tetraethyllead. More particularly, the invention relates to a new and improved process whereby tetraethyllead is manufactured by the ethylation of an active form of lead in a continuous manner.

Tetraethyllead may be synthesized by a number of reactions, a preferred procedure involving the ethylation of an alloy of lead and an alkali metal at elevated temperature with an ethylating agent. Typical of such operations is the ethylation of lead monosodium alloy with ethyl chloride, according to the equation:



The commercial process according to this reaction has consistently been carried out in batch operations. In such techniques, a quantity of sodium-lead alloy, NaPb, is charged to an autoclave, the alloy being in the form of comminuted granular solids. Heating and agitation of the autoclave contents is then started and ethyl chloride liquid feed is introduced. The ethyl chloride and alloy start reacting with increase in temperature, thereby increasing the pressure inside the reactor. The pressure is controlled by the rate of feed of the ethyl chloride. Upon completion of the ethyl chloride feed, the autoclave charge is maintained at the elevated temperature and pressure for further reaction. Excess ethyl chloride is then vaporized from the autoclave charge, the vaporization being facilitated by circulation of heating medium through a jacket on the autoclave.

The contents of the autoclave on completion of the cycle is a dry, powdered mass termed reaction mass, containing excess metallic lead, tetraethyllead, and sodium chloride, and minor amounts of sodium or sodium-lead alloy. The reaction mass is discharged to a steam still, wherein it is first immersed in water and then the tetraethyllead is steam distilled while the still charge is vigorously agitated.

According to the above method, the ethyl chloride is fed in the ratio of about one-half part by weight to one part of sodium-lead alloy. As already described, such a ratio of reactants, upon completion of the reaction, produces a dry, powdered mass. In the course of the above described steam distillation recovery method, frequent difficulty is encountered owing to agglomeration of the solid particles, which are predominantly lead. Such agglomeration tends to deposit lead sheets on the steam still, or to form balls or other massive forms of lead, which wedge the agitator and consequently interrupt the recovery operation.

The foregoing interruptions to the recovery op-

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eration is of course a deficiency of the former process. In addition, the process has been hampered by other deficiencies which have long been recognized and studied but not solved. A major disadvantage of the prior process lies in the fact that it is a batch operation and therefore subject to all the usual limitations of a batch operation. Such disadvantages include the thermal inefficiency arising from the cyclic variations in the temperature of the equipment. In addition, batch operations are notorious in requiring more operating labor than a continuous flow process. Furthermore, in batch operations, only a relatively minor fraction of the total time cycle is devoted to the actual reaction, a large percentage of the time being needed for charging, discharging, and the purification step of vaporizing excess ethyl chloride from the autoclave charge.

An object of the present invention is to provide a new and improved process capable of efficient continuous operation in the manufacture of tetraethyllead. Another important object is to assure high yields of tetraethyllead. An additional object is to virtually negate the possibility of decomposition of the tetraethyllead in the ethylation zone, and also to provide an ethylated mixture particularly susceptible to efficient recovery of the tetraethyllead therefrom. Yet another object is to provide a high production rate in terms of tetraethyllead produced per unit volume of reaction space.

Broadly defined, the invention comprises the ethylation of the lead of an alloy of lead and an alkali metal with a liquid ethylating agent, in the presence of a substantial excess of the ethylating agent. The mixture of components, or ethylation mixture, is stirred or agitated under non-ideal conditions; that is, the agitation is appreciably short of that required to provide uniform or ideal distribution of solids throughout the ethylation mixture. Although the solids in the ethylation zone are non-uniformly distributed, nevertheless a high fraction of about 90 percent or more are suspended by virtue of the agitation and all solids are in vigorous motion. In other words, the liquid proportions at all points is such that the solids do not impinge on each other with such frequency and force that mechanical working occurs. Such mechanical working has been found to result in cohesion of the solids into larger masses, and is attributed to the properties of lead which is a large component of the ethylation mixture solids.

Although the solids present are maintained in the described non-uniform state of distribution,

the liquid phase is maintained as a uniform homogeneous liquid. Thus the liquid phase is of invariant or identical composition at all points in the ethylation zone as precisely as can be determined.

The invention resides in part in the discovery that by non-ideal agitation of the reacting mixture one can achieve a segregation of the solid components of the mixture according to the degree of ethylation, but at the same time the tetraethyllead product is uniformly distributed through the predominantly ethyl chloride liquid phase. Surprisingly, the liquid phase does not show a composition gradient even when the lead containing alloy is fed cyclically. By cyclically is meant that the ethylation is carried out continuously but the alloy is fed intermittently in batches for greater convenience. Even under such conditions, we are unable to detect a stratification of the liquid phase in terms of the tetraethyllead content.

The advantages and best method of operating the process are more easily understood from the following description and example and the accompanying figure. The figure is a diagrammatic representation of apparatus for a preferred and easily operable embodiment of the process.

Referring to the figure, the principal unit of apparatus is the ethylation vessel or ethylator 1. The usual auxiliary equipment includes an ethyl chloride supply tank 2 and feed line 3, and an alloy supply hopper 4 fitted with lines 43, 44, for maintaining an inert gas atmosphere in contact with the alloy. A feed column 5, which can be blocked off by valves 6, 7, provides a pressurized feed chamber from which the comminuted alloy can be dropped into the feed end of conveyer 8. Provision is made for pressure blanketing of the alloy in feed chamber 5 by inert gas lines 45, 46. A drive motor 9 powers the conveyer, which transports the alloy into the ethylator 1 at the top, that is into a vapor space. The ethyl chloride feed rate through line 3 is controlled by valve 10, a flow meter 11 providing visual check on the rate of flow.

The ethylated mixture from the ethylator is discharged through one or more nozzles and valves of the outlet manifold assembly 12. Thus nozzle line 13₂ can be used for the discharge by opening valve 14₂. The discharged stream, regardless of which nozzle or tap it is released through, is passed through line 15, to a solids-liquid separator 16. A bottom discharge line 17 discharges solids, which include lead metal and alkali metal chlorides, to subsequent operations for the recovery of metal values. Removal of the liquid phase from the solids-liquid separator is accomplished through line 18, the flow rate to the tetraethyllead concentration apparatus 19 being controlled by valve 20. The concentration unit 19 may take several different forms, a preferred form being a low pressure fractionation column, wherein ethyl chloride is removed as an overhead product through line 21, the tetraethyllead being discharged as a pure or concentrated bottoms stream through line 22.

The ethylator 1 is a hemispherical bottomed vessel provided with a jacket 23 for a heat transfer medium introduced through line 24 and discharged through line 25. The heat transfer medium is conveniently made available at a desired temperature by mixing in blending valve 26, a supply of cold water introduced through line 27 and steam supplied by line 28.

Agitation elements within the ethylator in-

clude the propeller type agitators 29, 30, 31, and the bottom plate element 32, all these elements being mounted on shaft 33, driven by motor 34. This agitator assembly in operating stirs the mixture in the ethylator, including the alloy and reaction products, and the liquid phase. A vapor blow off line 36 from the ethylator provides for release of vapor when a decrease in pressure is necessary, either through pressure release line 37 and valve 38, or through the manually operated valve 39.

A bottom discharge valve 41 allows draining the ethylator through line 42 for cleanout. During operation, the level of the ethylation mixture is ascertainable from a liquid level gauge 40.

Wide variability in apparatus is possible, the process not being confined to any specific ethylation vessel. Thus, in large capacity installations it will be advantageous to use a plurality of agitating assemblies, each of relatively small sweep area in comparison with the cross sectional area of the ethylator. In such instances, the same results will be obtained and the process will benefit in that reliance is not placed on only one drive motor, as in the typical apparatus described above.

As the process is not limited to a particular form or composition of lead alloy, various alternatives to the feed equipment are available. Thus, instead of the feed equipment for solid comminuted alloy in the figure, an alternative arrangement can be easily substituted for feeding the alloy in the liquid or molten phase. In such case, the alloy feed apparatus will consist simply of a molten alloy supply tank and a feed line and nozzle for passing the liquid alloy to the ethylation zone.

The solids-liquid separator 16 may utilize any of several different unit operations. Thus, the ethylated slurry is susceptible of filtration, so that the solids-liquid separator can be a continuous filter of types available. Alternatively, it has also been discovered that ethylated mixtures can be resolved into a solids stream virtually free of tetraethyllead by lixiviation with a solvent, such as naphtha, benzene, or preferably, an alkyl chloride. Ethyl chloride itself is a highly effective solvent for the tetraethyllead. Accordingly, the solids-liquid separator can be an extraction operation in which the liquid phase is dissolved in ethyl chloride and separated from the solids with high efficiency.

The advantages and benefits of the process as well as the mode of operation are illustrated by the following working example. In the example, all flows and compositions are in parts or percentages by weight, except as otherwise specified.

Example

The ethylator 1 was charged with ethyl chloride through line 10. Hot water was circulated to the jacket 23 through line 24 until the charge was at a temperature of 85° C. Monosodium-lead alloy, in the form of thin flakes, which had been previously charged to the alloy feed column 5 was then charged by opening valve 7 and operating feed conveyer 8. Agitation of the charge was started immediately before alloy flow was started, the speed of rotation providing a peripheral velocity of 660 feet per minute.

Steady operation was soon achieved, the ethylator being discharged through a draw off line located approximately at the midpoint, that is 55 percent of the total depth of the ethylation

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mixture above the bottom point thereof. The ethyl chloride and sodium-lead alloy were fed at the weight ration of 5.0:1.0, ethyl chloride:alloy, corresponding to an excess of approximately 1700 percent of the ethyl chloride theoretically required. The volumetric feed rates in terms of pounds per hour per cubic foot of ethylation zone, amounted to 6.5 pounds of sodium-lead alloy.

Steady conditions were maintained for an extended period. The slurry withdrawn from the ethylator, by a series of analyses, had the following composition:

	Weight percent
Tetraethyllead -----	5.5
Ethyl chloride -----	79.0
Sodium chloride -----	4.0—
Lead -----	11.0+
Sodium (as NaPb) -----	0.5
	100.0

It will be seen from the above that the slurry consisted of a liquid phase containing about 6.5 percent tetraethyllead, and amounting to 84.5 percent. The solids, amounting to 15.5 percent, contained over 70 percent lead and about 26 percent sodium chloride. The liquid : solid ratio of the ethylated slurry was thus about 5.5.

In this operation, a residence time of 110 minutes was maintained, the ethylation mixture being at the temperature of 85° C. and a pressure of 110 pounds per square inch gauge throughout the operation. Power input to the agitator 33 was slightly less than 0.1 horsepower per cubic foot of ethylation mixture. The tetraethyllead was produced at the volumetric production rate of 2.15 pounds, a yield of 93.7 percent being obtained.

The ease of operation and high yields obtained by the process are evident from the foregoing example. In this specific run, the yield of 93.7 percent is about 5 percent higher than the yields in thousands of commercial batch ethylations. In numerous other runs by the present process similar yield improvements, of the order of several percent have been found on the basis of analysis of both liquid phase and total slurry samples. A satisfactory degree of reproducibility was shown by statistical treatment of the results.

The reason for the high yields obtained in the process are not fully understood, but a plausible theory has been developed on the basis of careful observation of numerous operations. Without intending the process to be limited by any theory as to the improvements effected, it yet appears that the formation of tetraethyllead is a stagewise chemical reaction. Apparently an intermediate complex of undefined composition is first formed, which is capable of further reaction to give either tetraethyllead, or alternatively, by-products which include and are evidenced by evolution of gaseous compounds. These gaseous compounds include methane, ethane, ethylene and butanes. Material balances on a series of ethylations by the present process showed that the amount of such by-products were reduced approximately 40 percent from the amount accompanying the conventional commercial ethylation procedure. Inasmuch as it has been shown that by-product formation is evidence of diversion of a proportionate amount of alkali metal from the desired formation of tetraethyllead, it is apparent that by the

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present invention, loss of alkali metal in by-product formation is reduced. It is therefore believed that the high yields of the process are a result of the uniform temperature at all points in the ethylation zone, and the uniform composition of the liquid phase. In prior ethylations, owing to the preponderance of solids in the ethylation mixture there was little or no opportunity for the liquid reaction products, including the tetraethyllead formed, to be removed or distributed away from the immediate locale of formation. As a result "hot spots" were frequently formed within the ethylation mixture which could result in either partial decomposition of tetraethyllead, or else diversion of the probable intermediate to by-product formation. In contrast, in the present process, the localized high concentrations of either tetraethyllead or intermediates are minimized and in addition a uniform temperature is maintained throughout the system.

A particular virtue of the process is that the residence time of the solid components of the ethylation mixture can be controlled at will and to some extent independently of the feed ratio of the ethylating liquid and the solids. The significance of this finding is that, for example, if a particularly "thin" product slurry is desired, nevertheless the ethylation mixture can be maintained with an appreciably high solids content and the benefits of an extended residence time attained. Thus, in operation according to the foregoing example, but withdrawing at the top of the ethylation mixture, a liquid : solid ratio of 2:1 is achieved within the ethylator. For the same feed rates as in the above example, then, an average residence time of about 150 minutes can be provided. As a practical matter, such an extended residence time is beyond the range required for the high yields described. In addition, for liquid : solid ratios in such a range, the agitation requirements become more complicated. In general, it has been found preferable not to fall below a liquid : solid weight ratio of 3:1 within the ethylation mixture. The upper limit of the preferred range is a liquid : solid ratio of 5:1. Operation below this range, in conjunction with the non-ideal agitation which is a characteristic of the process, results in mechanical attrition of the solids particles, which, being largely metallic lead, are susceptible to mechanical fusion to form masses which can bind the agitator operation.

As already stated, non-ideal agitation of the ethylation mixture is an essential characteristic of the process. On the other hand, sufficient agitation power input, efficiently used, is required to maintain all the solids present discretely dispersed in the liquid phase. By efficient agitation is meant that the mechanical horsepower input of the agitator assembly is distributed to various strata in the ethylation zone according to methods frequently used. Among the factors which affect the agitation efficiency are the area of sweep of rotating agitator elements, and the nearness of the lowest agitating element to the bottom of the ethylation zone. Satisfactory agitation can be achieved with agitation sweep area varying from about 10 to about 60 percent of the ethylation zone cross sectional area. In general, it is preferred to use agitating elements, which can be either propellers or turbine agitators, which sweep at least 40 percent of the ethylation zone cross sectional area. The lower ranges are avoided as higher radial speeds are

required for a given mechanical horsepower input, which in turn increases the mechanical loss at the sealing or entrance point for the agitator assembly.

With respect to the vertical position of the agitation elements, it has been found that in virtually all instances the lowermost element should be appreciably closer to the bottom of the ethylation zone than is common practice. Thus, frequently the lowermost turbine or propeller is within a distance of from one-fourth to one-half of its diameter to the bottom of the zone.

In most embodiments of the process, a total depth of ethylation mixture of at least several feet, and up to about four feet, will be employed. To assure distribution of some solids throughout this ethylation zone, a plurality of agitating elements is customarily provided. A desirable vertical disposition of such plural elements is at space intervals of about one-half to three-fourths of the diameter of such elements.

The power requirements of the process will of course depend to some extent on the mechanical losses in the drive mechanism and similar mechanical devices, such as the gland or seal at which the agitator shaft enters the enclosed ethylation zone. Measurement of such losses, however, has shown the actual horsepower requirements to the agitator shaft. Surprisingly, the minimum horsepower requirements did not vary with a reduction in liquid : solid ratio in the range of 4:1 to 2:1, but satisfactory agitation was achieved with a power input of approximately 0.1 horsepower per cubic foot of ethylation zone. As a general rule, power inputs of over 0.5 horsepower per cubic foot are avoided in order to assure the non-uniform distribution of solids essential to the process.

As mentioned above, a significant feature of the process is the control of the residence time of the solids within the ethylation zone. This is achieved by the removal or discharge of a product slurry at a point remote from the bottom of the ethylation vessel, which in turn takes advantage of the effects of the non-ideal agitation employed. It has been found that by non-uniform distribution of the solids, a segregation both in terms of weight concentration and in terms of chemical composition is attained.

As an example of the gradation of chemical composition of the solids, slurry samples were removed from an ethylator operated similarly to that described in the working example. The samples were removed at the bottom and at the midpoint, that is, at a point corresponding to 50 percent of the total depth of the ethylation mixture. The liquid : solid ratios at the bottom and midpoint were 1.6:1 and 4.9:1, respectively. Analyses of the solids in these samples also showed that the ethylation was only 79 percent complete at this point but was 87 percent complete at the midpoint. The solids in the product slurry contained a lower proportion of unreacted solids than either of the foregoing samples.

It is apparent from the foregoing that appropriate selection of the withdrawal point allows retention of the reacting materials within the ethylation zone until the desired degree of ethylation is attained. In general, it is preferred to discharge at or above the midpoint of the ethylation zone. For the maximum residence time an overflow discharge is used. An overflow discharge, however, requires a feed ratio of liquid : solid of the order of 5:1 or greater if the ratio within the ethylator is not to drop below the

preferred range of 3:1. For this reason a discharge point between the midpoint and the overflow level is frequently employed.

The process has thus far been primarily described with reference only to use of a single ethylator. The principles of the process are nevertheless applicable in multi-stage operations and the same benefits will be realized. In every case, the charge in a specific individual ethylation zone is agitated in a non-ideal fashion. Accordingly, in each stage the withdrawal of a discharge slurry at a point remote from the bottom utilizes such non-ideal agitation to segregate the solids within the ethylator according to the degree of ethylation.

The process is not limited to a specific ethylation reaction, but is applicable to ethylation reactions involving sodium-lead alloys of relatively high sodium content. For example, the process is applicable in the ethylation of alloys of the composition corresponding to the formula Na_2Pb , or with lesser and greater proportions of sodium. In addition, alloys with other alkali metal components are suitable feed components and similar benefits will be realized. For example alloys containing potassium, either as the sole alkali metal, or as a component of a ternary alloy, can be advantageously ethylated by the process.

Although ethyl chloride is the preferred ethylating agent, other ethylating agents may be substituted for the ethyl chloride and the benefits of the method will be realized, although in varying degree. Examples of alternative ethylating agents which can thus be substituted for the ethyl chloride are ethyl bromide, ethyl iodide, and diethyl sulfate. As a practical matter, ethyl chloride will be most widely used owing to the cheapness and availability of this chemical.

The foregoing description of the process illustrates the effectiveness with which the objects of the invention are attained. Having fully described the invention and the best manner in which it is carried out, what we claim is:

1. The continuous process of making tetraethyllead comprising feeding an alkali metal alloy of lead and a liquid ethylating agent to an ethylation zone, in the proportions of at least 2 parts by weight of ethylating agent to 1 part by weight of alloy, and ethylating therein, agitating the ethylation mixture only sufficiently to maintain the reacting and reacted solids in non-uniform distribution in a liquid comprising a solution of tetraethyllead in the ethylating agent, said liquid being of uniform composition throughout the ethylation zone, and withdrawing at a point remote from the bottom of the ethylation zone a slurry of solids in the liquid, said solids being more ethylated than the solids in the ethylation zone.

2. The continuous process of making tetraethyllead comprising feeding ethyl chloride and monosodium-lead alloy to an ethylation zone in proportions of at least 2 parts by weight of ethyl chloride to 1 part by weight of alloy, ethylating therein while agitating only sufficiently to maintain the reacting and reacted solids in non-uniform distribution in a liquid of uniform composition throughout the ethylation zone, the liquid comprising a solution of tetraethyllead in ethyl chloride, and withdrawing at a point remote from the bottom of the ethylation zone a slurry of solids in the liquid, the solids being higher in reacted solids content than the solids in the ethylation zone.

3. The continuous process of making tetra-

ethyllead comprising feeding ethyl chloride and monosodium-lead alloy to an ethylation zone in the proportions of at least 2 parts by weight of ethyl chloride to 1 part by weight of alloy, ethylating therein while agitating only sufficiently to maintain the reacting and reacted solids in non-uniform distribution in a liquid of uniform composition throughout the ethylation zone, the liquid comprising a solution of tetraethyllead in ethyl chloride, and withdrawing at a point in the upper 50 percent of the total depth of the ethylation zone a slurry of solids in the liquid, the solids being higher in reacted solids content than the average solids in the ethylation zone, the withdrawal point providing a liquid to solids weight ratio within the ethylation zone of at least 3:1.

4. The process of claim 2 further defined in that the monosodium-lead alloy is fed while in the molten state.

5. The process of claim 2 further defined in that the monosodium-lead alloy is fed in the form of comminuted solids.

6. In the process of ethylating lead by contacting particles of an alkali metal alloy of lead with a liquid ethylating agent, the improvement which comprises effecting the contacting in a

tank in which the reactants are proportioned with a large excess of liquid to keep the reaction mixture in the form of a slurry of solid particles in said liquid, agitating the reaction mixture sufficiently vigorously to cause the liquid to be substantially uniform in composition throughout, but not vigorously enough to cause all the solid particles to be uniformly distributed so that the less reacted particles are stratified under the action of gravity below the more reacted particles, and removing reaction products by making withdrawals of both solid and liquid from the upper portion of the reaction mixture.

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