Nov. 21, 1933. E. T. OLSON 1,935,914

PREPARATION OF AROMATIC ALDEHYDES

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Fig. 1

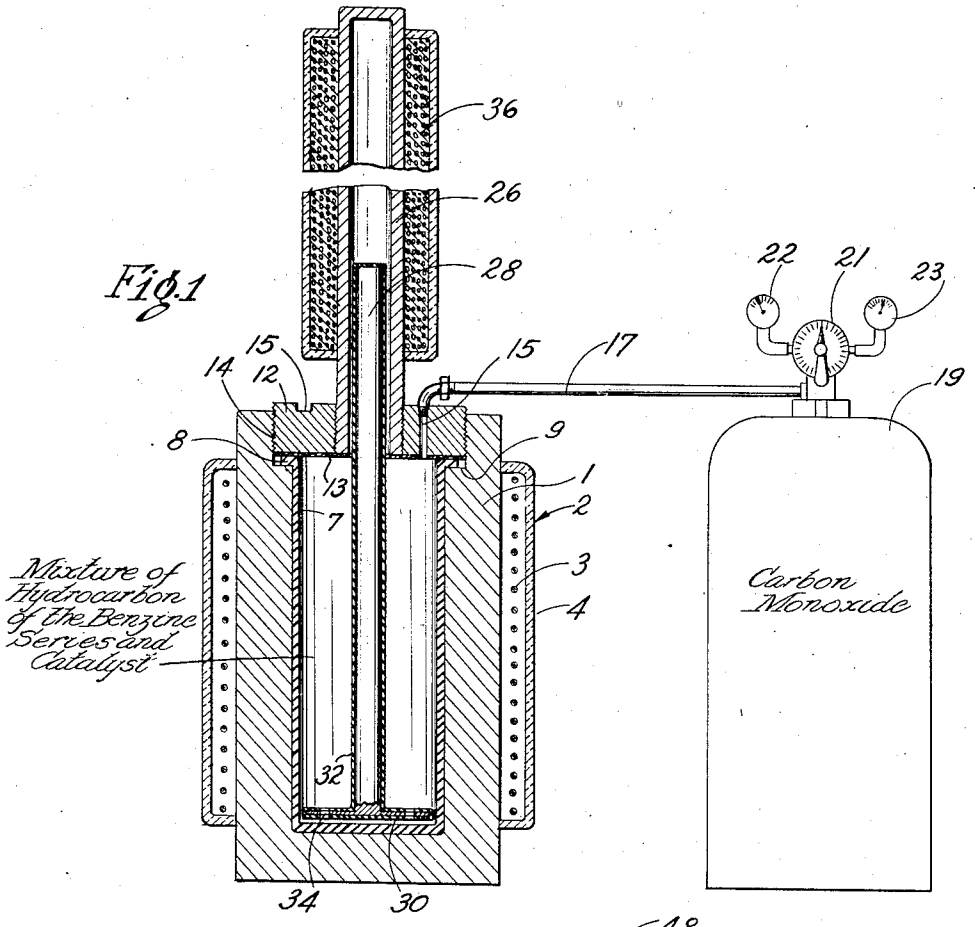
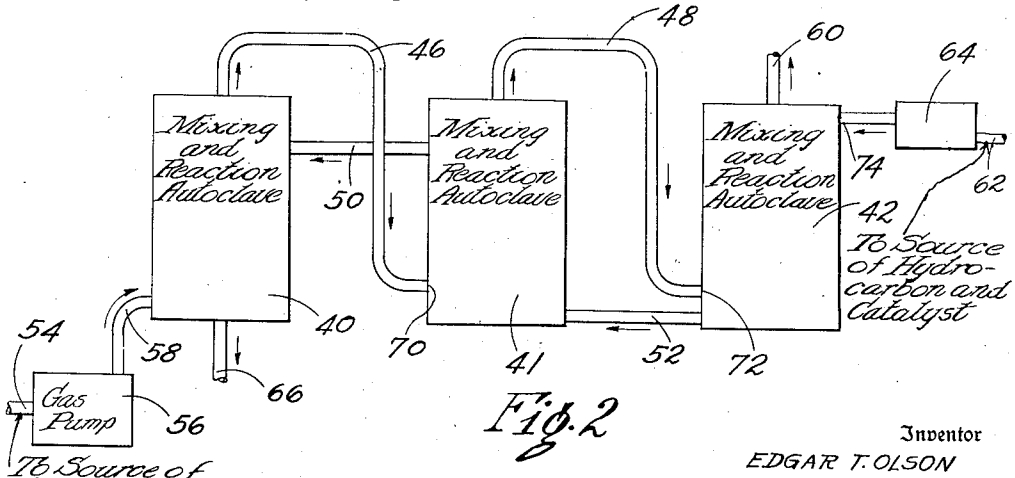


Fig. 2



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PREPARATION OF AROMATIC ALDEHYDES

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17 Claims. (Cl. 260—136)

The present invention relates to the synthesis of aromatic aldehydes from hydrocarbons of the benzene series or halogen derivatives thereof and more particularly is concerned with the manufacture of benzaldehyde from benzene.

Heretofore in the manufacture of aromatic aldehydes, comparatively expensive starting materials have been employed which are treated to a rather lengthy and necessarily expensive operation. For example in the production of benzaldehyde heretofore, toluene was the starting material which was chlorinated to benzyl chloride and hydrolyzed. The method was used to produce benzaldehyde, benzyl alcohol and benzoic acid and employed chlorine, toluene and suitable hydrolyzing acids.

According to the teaching of the present invention the above enumerated difficulties and objectional features, are avoided by the provision of an improved simplified process which adapts itself to commercial and continuous operation.

Briefly the invention consists in producing aldehydes by treating hydrocarbons of the benzene series or halogen derivatives thereof with carbon monoxide under pressure and in the presence of a suitable catalyst.

In practicing the invention various forms of apparatus can be employed, however, two forms of such apparatus are illustrated in the accompanying drawing wherein:

Figure 1 is a cross sectional view illustrating one form of apparatus for carrying out the present invention.

Fig. 2 is a diagrammatic view of apparatus for continuously producing aromatic aldehydes as taught in the present invention.

Referring to the drawing the numeral 1 indicates a heavy metal autoclave, which is surrounded by temperature control means, indicated generally at 2, which may comprise an electric resistance coil 3, covered by heat insulating material 4. The autoclave 1 is adapted to receive a non-corrodible container 7 which is adapted to slidably fit down into the autoclave 1 and which may be provided with a flange top 8 shaped to fit down against a shoulder portion 9 at the top of the tank 1. The tank 1 is provided with a cap 12 which may be removably secured in position by inter-engaging threaded portions 14 upon it and the tank 1, in which case sockets 15 for the reception of a spanner wrench (not shown) may be provided. A gasket 13 is ordinarily provided between the cap 12 and the upper end of the container 7 to insure a more perfect seal. The cap 12 is also formed with a suitably tapped aperture 16 in which is threaded a conduit 17 which extends to a tank 19 through the standard control valve 21 and pressure gauges 22, 23.

The cap 12 is formed with a threaded central aperture which receives a housing 26 which in turn slidably journals a cylindrical armature plunger 28 which has a stirring disk 30 secured to its lower end. The ram 28 and disk 30 are of iron or steel and in order to prevent corrosion are suitably plated over with a covering layer 32 of lead, copper, aluminum or other similar nontarnishing metals. The stirring disk 30 is formed with a plurality of apertures 34 which upon vertical reciprocating movement of the ram 28 and stirring disk 30 function to thoroughly stir any liquid in the container 7.

In order to reciprocate the stirring disk 30 and the shaft 28 which supports it, a solenoid coil 36 is provided around the housing 26 and the relation of parts is such that upon energizing, or de-energizing the solenoid 36 that the ram 28 and stirring disk 30 will be given a reciprocating up and down stirring movement in the container 7.

In employing the apparatus above described in the production of aromatic aldehydes the manufacture of benzaldehyde is typical and will be described. In this operation, a given quantity of benzene and the catalyst of aluminum chloride, are employed which quantities have the molar ratio of aluminum chloride to benzene of from .2 to 1 of the former to 1 of the latter, preferably in the neighborhood of from .33 to .5 of the former to 1 of the latter. These materials are mixed together and a certain percentage of water and also a percentage of benzaldehyde is added if necessary or preferred as hereafter described. The complete mix is then placed in the container 7, which is in turn lowered into the tank 1 whereupon the cap 12 with the gasket 13 thereunder is screwed into place to effectively seal the constituents of the reaction in the tank 1. Thereafter carbon monoxide, which is confined in the tank 19 under heavy pressure, is passed by way of control valve 21 through conduit 17 into the interior of the tank 1. The valve 21 is so regulated as to apply pressures of from 300 to 2000 pounds per square inch but preferably about 600 pounds to the interior of the tank. Thereafter the solenoid 36 is periodically energized to reciprocate the stirring means within the tank whereby the mixture of benzene and aluminum chloride and gaseous carbon monoxide is thoroughly and positively mixed.

The mixing operation is continued for from 15 minutes to 3 hours but preferably about 2 hours.

The temperature is controlled by the heating means 2 surrounding the tank 1 so as to keep the temperature during the mixing operation in the neighborhood of 25° to 50° C. preferably about 35° C.

The reaction which takes place is as follows:

$$C_6H_6+CO=C_6H_5CHO$$

As indicated the reaction appears to be reversible in nature and reaches an equilibrium when anywhere up to 80% of the benzene is converted into benzaldehyde. Generally when the operation is carried on with the various conditions being controlled to produce the best results a conversion in the neighborhood of 65% of benzene is good, particularly in commercial installations.

An important feature of the invention not fully discussed above is the mixing of a small amount, such as ½ to 3% of benzaldehyde, in the mixture of benzene and aluminum chloride prior to the stirring and conversion operation. By so doing it has been discovered that the time necessitated to reach an equilibrium is considerably reduced, apparently the benzaldehyde acting in itself as a catalyst. It has been found that the time can be reduced from approximately two hours to thirty minutes by way of example, if a percentage of the aldehyde to be obtained is initially mixed in the reaction constituents in the manner described.

Another important phase of the invention is the addition of a definite amount of water to the reacting materials. This water can be added as a definite measured amount to practically dry benzene, aluminum chloride, carbon monoxide or the amount of water in each one of these reaction constituents can be determined and the total amount of water present in the reaction chamber thereby controlled. It has been found that approximately 1 liter of water should be used to every 6 kilograms of aluminum chloride. This ratio when computed on the molar relation of aluminum chloride and benzene stated above is from about 4% to about 10% of the total weight. The amount of water may be maintained from about 0.25% to about 10%.

Referring to Fig. 2 of the drawing, the numerals 40, 41, and 42 indicate a series of autoclaves which are connected together by a plurality of conduits 46, 48, 50 and 52. A conduit 54 extends to a supply of carbon monoxide gas which is adapted to be forced by means of a pump 56 through conduit 58 into autoclave 40, through autoclave 40 into conduit 46, and autoclave 41, thence through conduit 46 into autoclave 42 from which it escapes to the atmosphere or to a storage or salvage means by way of conduit 60. A conduit 62 extends to a supply of the liquid reaction products which are forced into autoclave 42 of the system by pumps 64, through autoclave 42 into conduit 52, thence to autoclave 41 and from there to autoclave 40 by way of conduit 50. A conduit 66 is provided on the bottom portion of autoclave 40 to permit withdrawal of the reaction product. Check or one way valves may be provided if found necessary or desirable at the points 70, 72 and 74 or elsewhere in the system.

The apparatus described by the above and illustrated in Fig. 2 can be employed in the continuous manufacture of aromatic aldehydes and for the purpose of example the production of benzaldehyde is typical and will be described.

The benzene and the catalyst, aluminum chloride, are mixed substantially in the proportions discussed above under the description of the process as employed in conjunction with the apparatus shown in Fig. 1 and the determinate amount of water is added whereupon the materials are pumped by way of conduit 62 and pump 64 to the tank 42 from which they flow through conduit 52 into tank 41 and from there by way of conduit 50 into tank 40. Preferably monoxide gas is passed in a counter direction to the flow of liquid constituents through the tank system, as for example by way of conduits 54 and 58, tank 40, conduit 46, tank 41, conduit 48, tank 42 and conduit 60. The carbon monoxide is maintained under the pressure disclosed above by means of pump 56 and a release valve or pressure chamber is connected to conduit 60 as heretofore described.

The materials are ordinarily agitated in their passage through the autoclaves either by their counterflow as by the gas bubbling through the liquids or additionally by mechanical means such as those for example described in conjunction with Fig. 1.

The operation is preferably a continuous one with the reaction products ordinarily being drawn off in a constant manner by way of conduit 66 although this may if necessary be a periodic withdrawal. The various features in the operation of the continuous process are similar to those discussed above in conjunction with the batch process in that a small amount of benzaldehyde is preferably added to the constituents prior to their treating, also in that the temperature time and other features are substantially within the ranges described.

The products of the reaction of either the continuous or intermittent process can be separated to the individual compounds by any suitable chemical or mechanical method such as by hydrolysis and distillation. More specifically the products of the reaction containing the anhydrous aluminum chloride catalyst is mixed with water, with cooling. This results in a hydrated aluminum chloride solution which separates as a lower layer and can be drawn off from the upper layer consisting of benzaldehyde and unreacted benzene. This hydration and dissolving of the anhydrous aluminum chloride, which is accomplished in a tank equipped with an agitator and cooling coils, is accompanied by the evolution of heat. The reaction products may be added to the water, or the water to the reaction product, as may be desired.

The benzene in benzaldehyde is separated by fractional distillation. The separation by this method is relatively easy for the reason that the boiling point of benzene is 80 deg. C. while that of benzaldehyde is 180 deg. C. Any tars present in the washed benzene-benzaldehyde layer remain as a residue in the bottom of the still. The first fraction that comes off is a mixture of benzene and moisture,—the moisture being present due to the hydration process.

The benzaldehyde resulting from the above fractional distillation is a pure water white material containing 97 to 99.5% benzaldehyde. It is not subjected to any further drying or cleaning operation.

While the invention has been particularly described in conjunction with the production with benzaldehyde for which it is preferably employed it will be appreciated that substantially any aromatic aldehydes can be made from hydrocarbons of the benzene series in accordance with the teachings of the present invention. For example, toluene can be treated to obtain p-tolyladehyde, chlorbenzene can be treated to obtain chlorben-

zaldehyde, xylol can be treated to obtain xylolaldehyde, aniline can be treated to get amino benzaldehyde, nitro benzol to obtain nitrobenzaldehyde, etc.

It is also to be noted that the apparatus which has been described in conjunction with the present invention can take a plurality of forms as long as its function in combination with the process is preserved.

What I claim is:—

1. The synthesis of aromatic aldehydes which comprises treating hydrocarbons of the benzene series with carbon monoxide under pressures of 350 lb. to 2000 lb. per square inch, in the presence of aluminum chloride and 0.5% to 3% of the aldehyde.

2. The synthesis of aromatic aldehydes of hydrocarbons of the benzene series which comprises treating hydrocarbons with carbon monoxide in the presence of a plurality of catalysts and moisture.

3. The method of producing benzaldehyde which includes mixing aluminum chloride and benzene in the molar ratio of from 0.2 to 1 of the former to 1 of the latter, adding from .5% to 3% benzaldehyde, subjecting the mixture to the action of carbon monoxide at pressures ordinarily between 350 lb. sq. in. to 2000 lb. per square inch, and agitating the mixture while maintaining it approximately between 20° C. and 50° C. to thereby mix the materials and expedite the reaction.

4. The method of producing benzaldehyde which includes mixing aluminum chloride and benzene in the molar ratio of from 0.2 to 1 of the former to 1 of the latter, adding from .5% to 3% benzaldehyde, subjecting the mixture to the action of carbon monoxide at pressures ordinarily between 350 lb. sq. in to 2000 lb. sq. in. and agitating mixture.

5. The method of producing benzaldehyde which includes mixing aluminum chloride and benzene in the molar ratio of from 0.2 to 1 of the former to 1 of the latter, adding from .5% to 3% benzaldehyde, and subjecting the mixture to the action of carbon monoxide.

6. The method of producing benzaldehyde which includes mixing aluminum chloride and benzene in the molar ratio of from 0.2 to 1 of the former to 1 of the latter, subjecting the mixture to the action of carbon monoxide at pressures ordinarily between 250 lb. sq. in. to 2000 lb. sq. in., and agitating the mixture while maintaining it approximately between 20° C. and 50° C. to thereby mix the materials and expedite the reaction.

7. The method of producing benzaldehyde which includes mixing aluminum chloride and benzene, adding from .5% to 3% benzaldehyde, subjecting the mixture to the action of carbon monoxide at pressures ordinarily between 350 lb. sq. in. to 2000 lb. sq. in. and agitating the mixture while maintaining it approximately between 20° C. to 50° C. to thereby mix the materials and expedite the reaction.

8. The method of producing benzaldehyde which includes mixing aluminum chloride and benzene in the molar ratio of from 0.2 to 1 of the former to 1 of the latter, adding from about .25% to about 10% water, subjecting the mixture to the action of carbon monoxide and agitating the mixture to thereby mix the materials and expedite the reaction.

9. That method of making aromatic aldehydes from hydrocarbons of the benzene series which consists in mixing aluminum chloride with the hydrocarbon in molar ratio of .2 to 1. of the former to 1 of the latter, insuring over .5% of the aldehyde in the mixture, maintaining the presence of between about .25% and about 10% water in the mixture, treating with carbon monoxide under high pressures and agitating the mixture during the treatment to thereby mix the materials and expedite the reaction.

10. That method of making aromatic aldehydes from hydrocarbons of the benzene series which consists in mixing aluminum chloride with the hydrocarbon in molar ratio of .2 to 1. of the former to 1 of the latter, insuring over .5% of the aldehyde in the mixture, treating with carbon monoxide under high pressures and agitating the mixture during the treatment to thereby mix the materials and expedite the reaction.

11. That method of making aromatic aldehydes from hydrocarbons of the benzene series which consists in mixing aluminum chloride with the hydrocarbon, insuring the presence of from about .25% to about 10% water in the mixture, treating with carbon monoxide under high pressures and agitating the mixture during the treatment to thereby mix the materials and expedite the reaction.

12. A continuous method of producing aldehydes from hydrocarbons of the benzene series which comprises mixing aluminum chloride with the hydrocarbon in molar ratio of between .2 and 1. of the former to 1 of the latter insuring over .5% of the finished aldehyde in the mixture, maintaining the presence of between about .25% and about 10% of water in the mixture, continuously passing said mixture through a series of tanks, continuously passing carbon monoxide under a pressure of between 350 lb. sq. in. and 2000 lb. sq. in. through the tanks in a direction opposite to the flow of the mixture and continuously removing the reaction aldehyde from the tanks.

13. A continuous method of producing aldehydes from hydrocarbons of the benzene series which comprises mixing aluminum chloride with the hydrocarbon in molar ratio of between .2 and 1. of the former to 1 of the latter, maintaining the presence of between about .25% and about 10% water in the mixture, continuously passing said mixture through a series of tanks, continuously passing carbon monoxide under a pressure of between 350 lb. sq. in. and 2000 lb. sq. in. through the tanks in a direction opposite to the flow of the mixture and continuously removing the reaction products from the tanks.

14. A continuous method of producing aldehydes from hydrocarbons of the benzene series which comprises mixing aluminum chloride with the hydrocarbon, continuously passing said mixture through a container, continuously passing carbon monoxide through the container in a direction opposite to the flow of the mixture, insuring the presence of up to about 10% water in the container and continuously removing the reaction products from the container.

15. A continuous method of making benzaldehyde which includes the steps of mixing aluminum chloride and benzene in the molar ratio of between .2 and 1. of the former to 1 of the latter, insuring over .5% benzaldehyde in the mixture, insuring the presence of between about .25% and about 10% of water in the mixture, continuously passing the mixture through a series of tanks, continuously passing carbon monoxide at a pres-

sure between 350 lb. sq. in. and 2000 lb. sq. in. through the tanks in a direction opposite to the movement of the mixture, agitating the mixture to thereby mix the materials and expedite the reaction and removing portions of the benzaldehyde formed by the reaction.

16. A continuous method of making benzaldehyde which includes the steps of mixing aluminum chloride and benzene in the molar ratio of between .2 and 1. of the former to 1 of the latter, continuously passing the mixture through a container, continuously passing carbon monoxide at a pressure between 350 lb. sq. in. and 2000 lb. sq. in. through the container in a direction opposite to the movement of the mixture, agitating the mixture to thereby mix the materials and expedite the reaction and removing portions of the products formed by the reaction.

17. A continuous method of making benzaldehyde which includes the steps of mixing aluminum chloride and benzene, continuously passing the mixture through a tank, continuously passing carbon monoxide through the tank in a direction opposite to the movement of the mixture, agitating the mixture to thereby mix the materials and expedite the reaction and removing portions of the product formed by the reaction.

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