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(54) Title: PREPARATION OF POLYOXYMETHYLENE DIMETHYL ETHERS BY REACTION OF DIMETHYLETHER WITH FORMALDEHYDE OVER HETEROGENEOUS CATALYSTS

(57) Abstract

A particularly useful process which includes the steps of providing a source of formaldehyde, preferably formed by conversion of methanol in the presence of a catalyst comprising silver as an essential catalyst component; and contacting the source of formaldehyde and a predominantely dimethyl ether feedstream with a heterogeneous, condensation promoting catalyst capable of hydrating dimethyl ether under conditions of reaction sufficient to form an effluent comprising water, methanol, formaldehyde, dimethyl ether, and polyoxymethylene dimethyl ethers is disclosed. Unreacted dimethyl ether is recovered from the effluent and recycled to the formation of polyoxymethylene dimethyl ethers. The resulting dimethyl ether-free liquid mixture is heated in the presence of an acidic catalyst to convert at least the methanol and formaldehyde present to polyoxymethylene dimethyl ethers. Advantageously, methylal and higher polyoxymethylene dimethyl ethers are formed and separated in a catalytic distillation column. By including in the column an anion exchange resin, an essentially acid-free product is obtained which can be used directly as a blending component, or fractionated, as by further distillation, to provide more suitable components for blending into diesel fuel.

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PREPARATION OF POLYOXYMETHYLENE DIMETHYL ETHERS BY REACTION OF DIMETHYLETHER WITH FORMALDEHYDE OVER HETEROGENEOUS CATALYSTS

TECHNICAL FIELD

The present invention relates to production of organic compounds, particularly polyoxymethylene dimethyl ethers, which are suitable components for blending into fuel having improved qualities for use in diesel engines. More specifically, it relates to employing a heterogeneous, condensation promoting catalyst capable of hydrating dimethyl ether in conversion of dimethyl ether and formaldehyde to form a condensation effluent. A dimethyl ether-free mixture, separated form the effluent, is heated in a catalytic distillation column to convert methanol and formaldehyde present to methylal and higher polyoxymethylene dimethyl ethers and separate the methylal from the higher polyoxymethylene dimethyl ethers. Advantageously, the catalytic distillation column has a section containing an anion exchange resin whereby an essentially acid-free product is obtained which can be used directly as a blending component, or fractionated, as by further distillation, to provide more suitable components for blending into diesel fuel.

Integrated processes of the invention also provide their own source of formaldehyde. For example, a source which is an un-purified liquid stream derived from a mixture formed by oxidative dehydrogenation (oxy-dehydrogenation) of methanol using a catalyst based silver as an essential catalyst.

BACKGROUND OF THE INVENTION

Conversion of low molecular weight alkanes such as methane to synthetic fuels or chemicals has received increasing attention because low molecular weight alkanes are generally available from secure and reliable sources. For example, natural gas wells and oil wells currently produce vast quantities of methane. Reported methods for converting low molecular weight alkanes to more easily transportable liquid fuels and chemical feedstocks can be conveniently categorized as direct oxidative routes and/or as indirect syngas routes. Direct oxidative routes convert lower alkanes to products such as methanol, gasoline, and relatively higher molecular weight alkanes. In contrast, indirect syngas routes typically involve production of synthesis gas as an intermediate product.

Routes are known for converting methane to dimethyl ether. For example, methane is steam reformed to produce synthesis gas. Thereafter, dimethyl ether and methanol can be manufactured simultaneously from the synthesis gas, as described in U.S. Patent No. 4,341,069 issued to Bell et al. They recommend a dimethyl ether synthesis catalyst having copper, zinc, and chromium co-precipitated on a gamma-alumina base. Alternatively, methane is converted to methanol, and dimethyl ether is subsequently manufactured from methanol by passing a mixed vapor containing methanol and water over an alumina catalyst, as described in an article by Hutchings in New Scientist (3 July 1986) 35.

Formaldehyde is a very important intermediate compound in the chemical industry. The extreme reactivity of the formaldehyde carbonyl group and the nature of the molecule as a basic building block has made formaldehyde an important feedstock for a wide variety of industrially important chemical compounds. Historically, formaldehyde has found its largest volume of application in the manufacture of phenol-formaldehyde resins, urea-formaldehyde resins and other polymers. Pure formaldehyde is quite uncommon since it polymerizes readily. It was usually obtained as an aqueous solution such as formalin, which contains only about 40 percent formaldehyde. However, more recently, formaldehyde is usually transported as an item of commerce in concentrations of 37 to 50 percent by weight. A solid source of formaldehyde called paraformaldehyde is also commercially available.

Because of the reactivity of formaldehyde, its handling and separation require special attention. It is a gas above -19°C and is flammable or explosive in air at concentrations of about 7 to about 12 mol percent. Formaldehyde polymerizes with itself at temperatures below 100°C and more rapidly when water vapor or impurities are present. Since formaldehyde is usually transported in aqueous solutions of 50 percent by weight or lower concentration, producers have tended to locate close to markets and to ship the methanol raw material, which has a smaller volume.

It is known that some reactions may be carried out by means of catalytic distillation. In catalytic distillation, reaction and separation are carried out simultaneously in a distillation column with internal and/or external stages of contact with catalyst.

In U.S. Pat. No. 4,215,011, Smith, Jr. discloses a method for the separation of an isoolefin, preferably having four to six carbon atoms, from streams containing mixtures thereof with the corresponding normal olefin, wherein the mixture is fed into a reaction-distillation column containing a fixed-bed, acidic cation exchange resin and contacted with the acidic cation exchange resin to react the isoolefin with itself to form a dimer and the dimer is separated from the normal olefin, the particulate catalytic material, i.e., the acidic cation exchange resin, being contained in a plurality of closed cloth pockets, which pockets are arranged and supported in the column by wire mesh.

In U.S. Pat. No. 4,443,559, Smith, Jr. discloses a catalytic distillation structure which comprises a catalyst component associated intimately with or surrounded by a resilient component, which component is comprised of at least 70 vol. percent open space for providing a matrix of substantially open space. Examples of such resilient component are open-mesh, knitted, stainless wire (demister wire or an expanded aluminum); open-mesh, knitted, polymeric filaments of nylon, Teflon, etc.; and highly-open structure foamed material (reticulated polyurethane).

In U.S. Pat. No. 5,113,015, David A. Palmer, K. D. Hansen and K. A. Fjare disclose to a process for recovering acetic acid from methyl acetate wherein the methyl acetate is hydrolyzed to methanol and acetic acid via catalytic distillation.

In German Democratic Republic DD 245 868 A1 published May 20, 1987 in the text submitted by the applicant, preparation of methylal is carried out by reaction of methanol with trioxane, formalin or paraformaldehyde in the presence of a specific zeolite. Autoclave reactions of 1 to 8 hours are described using a zeolite of the "LZ40 type" with a ratio of silicon dioxide to alumina ratio of 78 at temperatures from 493 to 543 K. Methylal content of the product as high as 99.8 percent (without methanol) is reported for trioxane at 523 K for 3 hours. Reaction pressures did not exceed 5 MPa in the autoclave. Neither conversions nor selectivity are reported.

In U.S. Pat. No. 4,967,014, Junzo Masamoto, Junzo Ohtake and Mamoru Kawamura describe a process for formaldehyde production by reacting methanol with formaldehyde to form methylal, $CH_3OCH_2OCH_3$, and then oxidizing the resulting methylal to obtain formaldehyde. In the methylal formation step, a solution containing methanol, formaldehyde and water was brought into solid-liquid contact with a solid acid catalyst, and a methylal-rich component was recovered as a distillate. This process employs reactive distillation performed using a distillation column and multireaction units. The middle portion of the distillation column was furnished with stages from which the liquid components were withdrawn and pumped to the reactor units, which contained solid acid catalyst. The reactive solutions containing the resulting methylal were fed to the distillation column, where methylal was distilled as the overhead product.

Polyoxymethylene dimethyl ethers are the best known members of the dialkyl ether polymers of formaldehyde. While diethyl and dipropyl polyoxymethylene ethers have been prepared, major attention has been given to the dimethyl ether polymers. Polyoxymethylene dimethyl ethers make up a homologous series of polyoxymethylene glycol derivatives having the structure represented by use of the type formula indicated below:

$$CH_3O(CH_2O)_nCH_3$$

Chemically, they are acetals closely related to methylal, $CH_3OCH_2OCH_3$, which may be regarded as the parent member of the group in which n of the type formula equals 1. They are synthesized by the action of methanol on aqueous formaldehyde or polyoxymethylene glycols in the presence of an acidic catalyst just as methylal is produced. On hydrolysis they are converted to formaldehyde and methanol. Like other acetals, they possess a high degree of chemical stability. They are not readily hydrolyzed under neutral or alkaline conditions, but are attacked by even relatively dilute acids. They are more stable than the polyoxymethylene diacetates.

Due to the relatively small differences in the physical properties (melting points, boiling points, and solubility) of adjacent members in this series, individual homologs are not readily separated. However, fractions having various average molecular weight values have been isolated. The normal boiling point temperature of a fraction having average n of 2 in the type formula is reported as 91° to 93°C. Boiling points at atmospheric pressure calculated from partial pressure equations range from 105.0°C for n of 2, to 242.3°C for n of 5. (Walker, Joseph Frederic, "Formaldehyde", Robert E. Krieger Publishing Co., issued as No. 159 of American Chemical Society Monograph series (1975), pages 167-169)

Polyoxymethylene dimethyl ethers are prepared in laboratory scale by heating polyoxymethylene glycols or paraformaldehyde with methanol in the presence of a trace of sulfuric or hydrochloric acid in a sealed tube for 15 hours at 150°C, or for a shorter time (12 hours) at 165° to 180°C. Considerable pressure is caused by decomposition reactions, which produce carbon oxides, and by formation of some dimethyl ether. The average molecular weight of the ether products increases with the ratio of paraformaldehyde or polyoxymethylene to methanol in the charge. A high polymer is obtained with a 6 to 1 ratio of formaldehyde (as polymer) to methanol. In these polymers, the n value of the type formula $CH_3O(CH_2O)_nCH_3$ is greater than 100, generally in the range of 300 to 500. The products are purified by washing with sodium sulfite solution, which does not dissolve the true dimethyl ethers, and may then be fractionated by fractional crystallization from various solvents.

U.S. Patent No. 2,449,469 in the names of W. F. Gresham and R. E. Brooks reported obtaining good yields of polyoxymethylene dimethyl ethers containing 2 to 4 formaldehyde units per molecule. This procedure is carried out by heating methylal with paraformaldehyde or concentrated formaldehyde solutions in the presence of sulfuric acid.

In the past, various molecular sieve compositions, natural and synthetic, have been found to be useful for a number of hydrocarbon conversion reactions. Among these are alkylation, aromatization, dehydrogenation and isomerization. Among the sieves which have been used are Type A, X, Y and those of the MFI crystal structure as shown in "Atlas of Zeolite Structure Types," Second Revised Edition, 1987, published on behalf of the Structure Commission of the International Zeolite Associates and incorporated by reference herein. Representative of the last group are ZSM-5 and AMS borosilicate molecular sieves.

Prior art developments have resulted in the formation of many synthetic crystalline materials. Crystalline aluminosilicates are the most prevalent and, as described in the patent literature and in the published journals, are designated by letters or other convenient symbols. Exemplary of these materials are Zeolite A (Milton, in U.S. Patent No. 2,882,243), Zeolite X (Milton, in U.S. Pat. No. 2,882,244), Zeolite Y (Breck, in U.S. Patent No. 3,130,007), Zeolite ZSM-5 (Argauer, et al., in U.S. Patent No. 3,702,886), Zeolite ZSM-11 (Chu, in U.S. Patent No. 3,709,979), Zeolite ZSM-12 (Rosinski, et al., in U.S. Patent No. 3,832,449), and others.

It is well known that internal combustion engines have revolutionized transportation following their invention during the last decades of the 19th century. While others, including Benz and Gottleib Wilhelm Daimler, invented and developed engines using electric ignition of fuel such as gasoline, Rudolf C. K. Diesel invented and built the engine named for him which employs compression for autoignition of the fuel in order to utilize low-cost organic fuels. Development of improved diesel engines for use in automobiles has proceeded hand-in-hand with improvements in diesel fuel compositions, which today are typically derived from petroleum. Modern high performance diesel engines demand ever more advanced specification of fuel compositions, but cost remains an important consideration.

Even in newer, high performance diesel engines combustion of conventional fuel produces smoke in the exhaust. Oxygenated compounds and compounds containing few or no carbon-to-carbon chemical bonds, such as methanol and dimethyl ether, are known to reduce smoke and engine exhaust emissions. However, most such compounds have high vapor pressure and/or are nearly insoluble in diesel fuel, and they have poor ignition quality, as indicated by their cetane numbers. Furthermore, other methods of improving diesel fuels by chemical hydrogenation to reduce their sulfur and aromatics contents, also causes a reduction in fuel lubricity. Diesel fuels of low lubricity may cause excessive wear of fuel injectors and other moving parts which come in contact with the fuel under high pressures.

Recently, U.S. Patent No. 5,746,785 in the names of David S. Moulton and David W. Naegeli reported blending a mixture of alkoxy-terminated poly-oxymethylenes, having a varied mixture of molecular weights, with diesel fuel to form an improved fuel for autoignition engines. Two mixtures were produced by reacting paraformaldehyde with (i) methanol or (ii) methylal in a closed system for up to 7 hours and at a temperatures of 150° to

240°C and pressures of 300 psi to 1,000 psi to form a product containing methoxy-terminated poly-oxymethylenes having a molecular weight of from about 80 to about 350 (polyoxymethylene dimethyl ethers). More specifically, a 1.6 liter cylindrical reactor was loaded with a mixture of methanol and paraformaldehyde, in molar ratio of about 1 mole methanol to 3 moles paraformaldehyde, and in a second preparation, methylal (dimethoxymethane) and paraformaldehyde were combined in a molar ratio of about 1 mole methylal to about 5 moles paraformaldehyde. In the second procedure, a small amount of formic acid, about 0.1 percent by weight of the total reactants, was added as a catalyst. The same temperatures, pressures and reaction times are maintained as in the first. Disadvantages of these products include the presence of formic acid and thermal instability of methoxy-terminated poly-oxymethylenes under ambient pressure and acidic conditions.

There is, therefore, a present need for catalytic processes to prepare oxygenated organic compounds, particularly polyoxymethylene dimethyl ethers, which do not have the above disadvantages. An improved process should be carried out advantageously in the liquid phase using a suitable condensation-promoting catalyst system, preferably a molecular sieve based catalyst which provides improved conversion and yield. Such an improved process which converts lower value compounds to higher polyoxymethylene dimethyl ethers would be particularly advantageous. Dimethyl ether is, for example, less expensive to produce than methanol on a methanol equivalent basis, and its condensation to polyoxymethylene dimethyl ethers does not produce water as a co-product.

The base diesel fuel, when blended with such mixtures in a volume ratio of from about 2 to about 5 parts diesel fuel to 1 part of the total mixture, is said to provide a higher quality fuel having significantly improved lubricity and reduced smoke formation without degradation of the cetane number or smoke formation characteristics as compared to the base diesel fuel.

This invention is directed to overcoming the problems set forth above in order to provide Diesel fuel having improved qualities. It is desirable to have a method of producing a high quality diesel fuel that has better fuel lubricity than conventional low-sulfur, low-aromatics diesel fuels, yet has comparable ignition quality and smoke generation characteristics. It is also desirable to have a method of producing such fuel which contains an additional blended component that is soluble in diesel fuel and has no carbon-to-carbon bonds. Furthermore, it is desirable to have such a fuel wherein the concentration of gums and other undesirable products is reduced.

SUMMARY OF THE INVENTION

Economical processes are disclosed for production of a mixture of oxygenated organic compounds which are suitable components for blending into fuel having improved qualities for use in compression ignition internal combustion engines (diesel engines).

According to the present invention, there is now provided a continuous process for catalytic production of oxygenated organic compounds, particularly polyoxymethylene dimethyl ethers. More specifically, continuous processes of this invention include contacting a source of formaldehyde and a predominately dimethyl ether feedstream comprising dimethyl ether and methanol with a condensation promoting catalyst capable of hydrating dimethyl ether, in a form which is heterogeneous to the feedstream, under conditions of reaction sufficient to form an effluent of the condensation comprising water, methanol, formaldehyde, dimethyl ether, one or more polyoxymethylene dimethyl ethers having a structure represented by the type formula

$$CH_3O(CH_2O)_nCH_3$$

in which formula n is a number from 1 to about 10.

For this aspect of the invention, suitable condensation-promoting catalysts include at least one member of the group consisting of molecular sieves. A preferred class of molecular sieve is crystalline metallosilicates exhibiting the MFI crystal structure, such as crystalline aluminosilicates and crystalline borosilicates. More preferably the molecular sieve is crystalline aluminosilicate exhibiting the MFI crystal structure with a silicon-to-aluminum atomic ratio of at least 10, or the molecular sieve is crystalline borosilicate exhibiting the MFI crystal structure, and has the following compositions in terms of mole ratios of oxides:

$$0.9 \pm 0.2\ M_{2/n}O : B_2O_3 : Y\,SiO_2 : Z\,H_2O,$$

wherein M is at least one cation having a valence of n, Y is between 4 and about 600, and Z is between 0 and about 160.0.

In another aspect, this invention provides continuous processes which further comprise fractionating the effluent of the condensation to obtain an overhead stream which is predominantly dimethyl ether, and an essentially dimethyl ether-free bottom stream comprising formaldehyde, methanol and at least methylal. Preferably at least a portion of the overhead stream containing dimethyl ether is recycled to contacting with the condensation-promoting catalyst.

According to a further aspect of this invention, the essentially dimethyl ether-free bottom stream comprising formaldehyde, methanol and at least methylal is heated with an acidic catalyst, which is heterogeneous to the feedstream, under conditions of reaction sufficient to convert formaldehyde and methanol present to methylal and higher polyoxymethylene dimethyl ethers.

Preferably, the heating of the bottom stream with the acidic catalyst employs at least one catalytic distillation column with internal and/or external stages of contact with the acidic catalyst, and internal zones to separate the methylal from the higher polyoxymethylene dimethyl ethers.

Suitable acidic catalysts include at least one member of the group consisting of bentonites, montmorillonites, cation-exchange resins, and sulfonated fluoroalkylene resin derivatives, preferably comprises a sulfonated tetrafluoroethylene resin derivative. A preferred class of acidic catalysts comprises at least one cation-exchange resin of the group consisting of styrene-divinylbenzene copolymers, acrylic acid-divinylbenzene copolymers, and methacrylic acid-divinylbenzene copolymers. Preferably, the heating of the bottom stream with the acidic catalyst employs at least one distillation column with internal and/or external stages of contact with the acidic catalyst.

Advantageously, the mixture of polyoxymethylene dimethyl ethers is contacted with an anion exchange resin to form an essentially acid-free mixture. Contacting with the anion exchange resin is preferably carried out within a section of the catalytic distillation column below the stages of contact with the acidic catalyst to form an essentially acid-free mixture.

In a preferred embodiment of the invention the essentially acid-free mixture of polyoxymethylene dimethyl ethers is fractionated within a section of the distillation column below the stages of contact with the acidic catalyst to provide an aqueous side-stream which is withdrawn from the distillation column, and an essentially water-free mixture of higher molecular weight polyoxymethylene dimethyl ethers (values of n greater 1) which is withdrawn from the distillation column near its bottom. Advantageously, at least a portion of the aqueous side-stream is used for recovery of an aqueous formaldehyde solution in an adsorption column.

Integrated processes of the invention also provide their own source of formaldehyde. For example, a source which is an un-purified liquid stream derived from a mixture formed by oxidative dehydrogenation (oxy-dehydrogenation) of methanol by a process comprising continuously contacting a gaseous feedstream comprising methanol, dioxygen and diluent gas with a catalytically effective amount of an oxidative dehydrogenation promoting catalyst comprising silver as an essential catalyst component at elevated temperatures to form a gaseous mixture comprising formaldehyde, methanol, dioxygen, diluent gas, carbon dioxide and water vapor; cooling the gaseous mixture to predominantly condense water and adsorb formaldehyde therein; and separating the resulting liquid source of formaldehyde from a mixture of gases comprising methanol, dioxygen, diluent gas, carbon dioxide and water vapor.

The contacting of the gaseous feedstream with the oxidative dehydrogenation promoting catalyst is carried out at temperatures in a range from about 500° to about 700°C, preferably from about 550° to about 650°C, and more preferably from about 590° to about 620°C.

The integrated process provides for recovery of the formaldehyde formed as an aqueous solution preferably containing from about 5 to about 25 percent methanol and less than about 40 percent water by using at least one continuous adsorption column with cooling. Preferably the formaldehyde formed is recovered as an aqueous solution containing less than about 40 percent water, preferably less than about 50 percent water and more preferably less than about 25 percent water by using at least one continuous adsorption column with cooling to temperatures in a range downward from about 100°C to 15°C.

Suitable sources of dioxygen are air or a dioxygen-enriched gas stream obtained by physically separating a gaseous mixture containing at least about 10 volume percent dioxygen into a dioxygen-depleted stream and a dioxygen-enriched gas stream. Preferably the gaseous mixture contains at least 60 volume percent dinitrogen and wherein the dioxygen-enriched gas stream comprises a volume ratio of dinitrogen to dioxygen of less than 2.5 to 1.

For this aspect of the invention, suitable oxidative dehydrogenation promoting catalyst comprises silver and optionally up to about 8 percent by weight of a compound selected from the group consisting of oxides of boron, phosphorous, vanadium, selenium, molybdenum and bismuth, phosphoric acid, ammonium phosphate and ammonium chloride.

For a more complete understanding of the present invention, reference should now be made to the embodiments illustrated in greater detail in the accompanying drawing and described below by way of examples of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURES 1 to 6 are schematic flow diagrams depicting preferred aspects of the present invention for continuous catalytic production of polyoxymethylene dimethyl ethers by chemical conversion of dimethyl ether, methanol and formaldehyde over a heterogeneous, condensation promoting catalyst capable of hydrating dimethyl ether in conversion of dimethyl ether and formaldehyde to form a condensation effluent. Unreacted dimethyl ether is recovered from the effluent for recycling, and a resulting dimethyl ether-free liquid mixture is heated in a catalytic distillation column with internal stages of contact to convert formaldehyde and methanol present to methylal and higher polyoxymethylene dimethyl ethers. This reaction mixture is contacted with an anion exchange resin to form an essentially acid-free product mixture and fractionated to provide suitable components for blending into diesel fuel.

The source of formaldehyde in the integrated process depicted in FIGURE 1 (28) is a stream of formaldehyde and methanol derived from dehydrogenation of dimethyl ether over a catalyst consisting of copper, zinc and a member selected from the group consisting of sulfur, selenium and tellurium as catalyst components.

The source of formaldehyde in the integrated process depicted in FIGURE 2 (29) is a stream of formaldehyde in methanol derived from dehydrogenation of methanol over a catalyst consisting of copper, zinc and a member selected from the group consisting of sulfur, selenium and tellurium as catalyst components.

The source of formaldehyde in the integrated process depicted in FIGURE 3 (30) is a stream of aqueous formaldehyde in methanol derived from oxidation of dimethyl ether over of an oxidation promoting catalyst comprising tungsten oxide. In this aspect of invention, recycle gas from the formaldehyde absorber is combined with air, mixed with dimethyl ether, preheated against reactor product, and then fed to the formaldehyde reactor.

The source of formaldehyde in the integrated process depicted in FIGURE 4 (31) is a stream of aqueous formaldehyde in methanol derived from oxidative dehydrogenation of dimethyl ether over an oxidative dehydrogenation promoting catalyst comprising silver as an essential catalyst component. In this aspect of invention, recycle gas from the formaldehyde absorber is combined with air, mixed with dimethyl ether, preheated against reactor product, and then fed to the formaldehyde reactor

The source of formaldehyde in the integrated process depicted in FIGURE 5 (32) is a stream of formaldehyde in methanol derived from oxidation of methanol over an oxidation promoting catalyst comprising oxides of molybdenum as an essential catalyst components.

The source of formaldehyde in the integrated process depicted in FIGURE 6 (33) is a stream of aqueous formaldehyde derived from oxidative dehydrogenation of methanol over a catalyst comprising silver as an essential catalyst component at elevated temperatures.

GENERAL DESCRIPTION

The improved processes of the present invention employ a heterogeneous, condensation promoting catalyst capable of hydrating dimethyl ether in conversion of dimethyl ether and formaldehyde to form a condensation effluent. In general, after the feedstream is passed over the catalyst it will contain a mixture of organic oxygenates at least one of which is of higher molecular weight than the starting dimethyl ether. For example, effluent mixtures can comprise water, methanol, formaldehyde, dimethyl ether, methylal and other polyoxymethylene dimethyl ethers having a structure represented by the type formula

$$CH_3O(CH_2O)_nCH_3$$

in which formula n is a number ranging between 1 and about 15, preferably between 1 and about 10. More preferably the mixture contains a plurality of polyoxymethylene dimethyl ethers having values of n in a range from 2 to about 7. Conditions of reaction include temperatures in a range from about 50° to about 300°C, preferably in a range from about 150° to about 250°C.

Stoichiometry of this condensation may be expressed by the following equations;

$$CH_3OCH_3 + n\,CH_2O \Longrightarrow CH_3O(CH_2O)_nCH_3$$

$$2\,CH_2OH + m\,CH_2O \Longrightarrow CH_3O(CH_2O)_mCH_3 + H_2O$$

which may be combined as in the following equation when n is equal to m;

$$CH_3OCH_3 + 2\,CH_3OH + 2n\,CH_2O \Longrightarrow 2\,CH_3O(CH_2O)_nCH_3 + H_2O$$

As shown above, the synthesis of methylal and higher polyoxymethylene dimethyl ethers from dimethyl ether, methanol, and formaldehyde is a reversible reaction that yields water as a co-product. Under certain conditions at least a portion of the water may be consumed in a dehydrogenation reaction expressed by the following equations;

$$CH_3OCH_3 + CH_3OH + H_2O \dashrightarrow 3\,CH_2O + 3\,H_2$$

and

$$CH_3OCH_3 + H_2O \Longleftrightarrow 2\,CH_3OH$$

Sources of dimethyl ether useful herein are predominantly dimethyl ether, preferably at least about 80 percent dimethyl ether by weight, and more preferably about 90 percent dimethyl ether by weight. Suitable dimethyl ether sources may contain other oxygen containing compounds such as alkanol and/or water, preferably not more than about 20 percent methanol and/or water by weight, and more preferably not more than about 15 percent methanol and/or water by weight.

According to the present invention, the ratio of formaldehyde to dimethyl ether in the feedstreams is any mole ratio which results in the production of the desired oxygenated organic compound. The ratio of formaldehyde to dimethyl ether is preferably between about 10:1 and about 1:10 moles. The ratio of formaldehyde to dimethyl ether is preferably between about 5:1 and about 1:5 moles. More preferably, the ratio of formaldehyde to dimethyl ether is between about 2: 1 and about 1:2 moles.

The process can be performed at any temperature and pressure at which the reaction proceeds. Preferred temperatures are between about 20° and about 150° C,with between about 90° and about 125° C being more preferred. The most preferred temperatures are between about 115° and about 125° C.

The pressure can be atmospheric or super-atmospheric pressure. Preferred pressures are, according to the present invention, between about 1 and about 100 atmospheres, with between about 15 and about 25 atmospheres being most preferred.

The reaction mixture feed gas flow rate, expressed as gas hourly space velocity, can be between about 50 and about 50,000 hr^{-1}, most preferably, between about 100 and about 2,000 hr^{-1}. Un-converted dimethyl ether can be recovered from the mixture by methods well known in the art. One particularly desirable method is the use of distillation of the condensed product.

The process of this invention can be performed in either a fixed or fluid bed reactor, using either continuous or batch processing methods. It is preferred to use a fixed bed reactor and a continuous mode of operation.

Broadly, according to the present invention, a catalyst system is provided which comprises at least one molecular sieve, preferably a crystalline metallosilicate exhibiting the MFI crystal structure. Generally the crystalline metallosilicate is combined with active or inactive materials, synthetic or naturally occurring zeolites, as well as inorganic or organic materials which would be useful for binding the crystalline metallosilicate. Other well-known materials include mixtures of silica, silica-alumina, alumina sols, clays, such as bentonite or kaolin, or other binders well known in the art. The crystalline metallosilicate can also be mixed intimately with porous matrix materials, such as silica-magnesia, silica-alumina, silica-thoria, or silica-titania. The crystalline metallosilicate content can vary anywhere from a few up to 100 percent by weight of the total finished product. Typical catalytic compositions contain about 5 percent to about 80 percent by weight of the crystalline metallosilicate

Generally, the term "molecular sieve" includes a wide variety of positive ion-containing crystalline materials of both natural and synthetic varieties. They are generally characterized as crystalline aluminosilicates, although other crystalline materials are included in the broad definition. The crystalline aluminosilicates are made up of networks of tetrahedra of SiO_4 and AlO_4 moieties in which the silicon and aluminum atoms are cross-linked by the sharing of oxygen atoms. The electrovalence of the aluminum atom is balanced by the use of positive ions such as alkali metal or alkaline earth metal cations.

Zeolitic materials useful herein, both natural and synthetic, have been demonstrated in the past to have catalytic capabilities for many hydrocarbon processes. Zeolitic materials, often referred to as molecular sieves, are ordered porous crystalline aluminosilicates having a definite structure with large and small cavities interconnected by channels. The cavities and channels throughout the crystalline material are generally uniform in size allowing selective separation of hydrocarbons. Consequently, these materials in many instances have come to be classified in the art as molecular sieves and are utilized, in addition to the selective adsorptive processes, for certain catalytic properties. The catalytic properties of these materials are also affected, to some extent, by the size of the molecules which are allowed selectively to penetrate the crystal structure, presumably to be contacted with active catalytic sites within the ordered structure of these materials.

Manufacture of the ZSM materials utilizes a mixed base system in which sodium aluminate and a silicon-containing material are mixed together with sodium hydroxide and an organic base, such as tetrapropylammonium hydroxide and tetrapropylammonium bromide, under specified reaction conditions to form the crystalline aluminosilicate.

A preferred class of useful molecular sieves, according to the present invention, are crystalline borosilicate molecular sieves disclosed in commonly assigned U.S. Patent No. 4,268,420, U.S. Patent No. 4,269,813, U.S. Patent No. 4,292,457, and U.S. Patent No. 4,292,458 to Marvin R. Klotz, which are incorporated herein by reference.

Suitable for use according to the present invention are, broadly, crystalline borosilicates which comprise a molecular sieve material having the following compositions in terms of mole ratios of oxides:

$$0.9\pm0.2\ M_{2/n}O : B_2O_3 : Y\,SiO_2 : Z\,H_2O,$$

where M is at least one cation having a valence of n, Y is between 4 and about 600, and Z is between 0 and about 160.

Embodiments of such borosilicate provide an X-ray diffraction pattern comprising the following X-ray diffraction lines:

d (Å)	Assigned Strength
11.2 ± 0.2	W-VS
10.0 ± 0.2	W-MS
5.97±0.07	W-M
3.82±0.05	VS
3.70±0.05	MS
3.62±0.05	M-MS
2.97±0.02	W-M
1.99±0.02	VW-M

wherein the assigned strengths correspond to the following values of relative peak heights:

Assigned Strength	Relative Peak Height
VW	less than 10
W	10-19
M	20-39
MS	40-70
VS	greater than 70

and "d" represents interplanar spacings, expressed in terms of Angstrom units. A range of assigned strengths comprises all strengths between the limits shown.

Embodiments of these borosilicates are prepared by the method which comprises: (1) preparing a mixture containing an oxide of silicon, an oxide of boron, a hydroxide of an alkali metal or an alkaline earth metal, an alkyl ammonium cation or a precursor of an alkyl ammonium cation, and water; and (2) maintaining said mixture at suitable reaction conditions to effect formation of said borosilicate, said reaction conditions comprising a reaction temperature within the range of about 25° to about 300°C, a pressure of at least the vapor pressure of water at the reaction temperature, and a reaction time that is sufficient to effect crystallization.

After recovering a dimethyl ether-free mixture form the condensation effluent, the mixture is heated in a catalytic distillation column with an acidic catalyst, which is heterogeneous to the feedstream, under conditions of reaction sufficient to convert formaldehyde and methanol present to methylal and higher polyoxymethylene dimethyl ethers. Examples of the solid acidic catalyst for use in the present invention include cation exchange resins, sulfonated fluoroalkylene resin derivatives, and crystalline aluminosilicates.

Cation exchange resins that can be used in the present invention may be carboxylated or sulfonated derivatives, but sulfonated derivatives are preferred because of the high reaction yield that can be attained. Ion exchange resins that can be used may be gel-type cation exchange resins or macroporous (macroreticular) cation-exchange resins, but the latter as exemplified by Amberlite 200C of Organc Co, Ltd. and Lewalit SP112 of Bayer A.G. are preferred because of the high reaction yield that can be attained. Specific examples of useful ion exchange resins include a styrene-divinylbenzene copolymer, an acrylic acid-divinylbenzene copolymer, a methacrylic acid-divinylbenzene copolymer, etc.

A sulfonated tetrafluoroethylene resin derivative (trade name, Naflon H) is preferably used as a sulfonated fluoroalkylene resin derivative.

The most desirable of these solid acidic catalysts are macroreticular cation exchange resins having sulfonate groups.

According to the present invention, the ratio of formaldehyde to dimethyl ether in the feedstreams is any mole ratio which results in the production of the desired oxygenated organic compound. The ratio of formaldehyde to dimethyl ether is preferably between about 10:1 and about 1:10 moles. The ratio of formaldehyde to dimethyl ether is preferably between about 5:1 and about 1:5 moles. More preferably, the ratio of formaldehyde to dimethyl ether is between about 2:1 and about 1:2 moles.

According to an integrated process of the invention a source of formaldehyde is formed by subjecting methanol in the vapor phase to continuously contacting with dioxygen and diluent gas and a catalytically effective amount of an an oxidative dehydrogenation promoting catalyst comprising silver as an essential catalyst component at elevated temperatures to form a gaseous mixture comprising formaldehyde, methanol, dioxygen, diluent gas, carbon dioxide and water vapor; cooling the gaseous mixture to predominantly condense water and adsorb formaldehyde therein; and separating the resulting liquid source of formaldehyde from a mixture of gases comprising methanol, dioxygen, diluent gas, carbon dioxide and water vapor.

The ratio of dioxygen to methanol is, according to the present invention, any mole ratio which results in the production of the desired source of formaldehyde. The ratio of dioxygen to methanol is preferably between about 1:1 and about 1:1000 moles. More preferably, the ratio of dioxygen to dimethyl ether is between about 1: 1 and about 1:100 moles. Most preferably, the ratio of dioxygen to dimethyl ether is between about 1:1 and about 1:10 moles.

The dioxygen can be added to the reaction mixture as pure molecular oxygen, or diluted with an inert gas such as nitrogen or argon. It is preferred to keep the dioxygen at no more than 10 mole percent of the entire reaction feed so as to avoid the formation of explosive mixtures.

The Karl Fischer process, developed in the early 1900s by Karl Fischer Apparate and Rohrleitungsbau of Germany, is probably the most widely used silver catalyst process.

Several features distinguish this type of process from those catalyzed by metal oxides. Whereas the metal oxide processes achieve an overall yield of about 93 percent, commercial silver catalyzed units are generally believed to achieve an overall yield of about 88 percent. Per-pass methanol conversion is about 80 percent, with 90 percent selectivity to formaldehyde. The silver-catalyzed process operates with an excess of methanol and requires a specialized piece of equipment, such as a packed tower or a methanol boiler equipped with a special air mixer, to generate the methanol-air feed mixture. Since less air is used, however, equipment sizes are smaller and power consumption is less than for the metal oxide process.

The silver-catalyzed reaction is endothermic; but depending on the amount of feed preheat and air added, the exothermic reaction of oxygen with hydrogen sustains the reaction at temperatures in excess of 550°C. Steam can then be generated by cooling the reactor effluent before it is fed to the absorber. However, the steam has a lower pressure (about 30 psig), and the amount produced is insufficient to satisfy process steam requirements. This steam deficit is offset by the fuel value of the substantial amount of hydrogen (more than 18 vol percent) that remains in the absorber off-gas. If the absorber offgas is processed in a thermal oxidizer, a blower for additional combustion air is required, but a substantial amount of 200 psig steam may be produced.

The ratio of dioxygen to total methanol is, according to the present invention, any mole ratio which results in the production of the desired source of formaldehyde.

The ratio of dioxygen to methanol is preferably between about 1:1 and about 1:1000 moles. More preferably, the ratio of dioxygen to dimethyl ether is between about 1: 1 and about 1:100 moles. Most preferably, the ratio of dioxygen to dimethyl ether is between about 1:1 and about 1:10 moles.

The dioxygen can be added to the reaction mixture as pure molecular oxygen, or diluted with an inert gas such as nitrogen or argon. It is preferred to keep the dioxygen at no more than 10 mole percent of the entire reaction feed so as to avoid the formation of explosive mixtures.

According to the present invention, within the oxidation reaction zone methanol is oxidized with a source of dioxygen in the presence of an oxy-dehydrogenation catalytic composition containing, as an essential ingredient, silver with or without up to about 10 percent of a supplemental inorganic compound based upon the total weight of metal oxide and supplemental inorganic compounds. Suitable oxy-dehydrogenation catalysts have been developed for converting methanol with a source of dioxygen to produce formaldehyde, as described in U.S. Patent Number 5,401,884, U.S. Patent Number 5,102,838, U.S. Patent Number 4,786,743, U.S. Patent Number 4,521,618, U.S. Patent Number 4,474,996 and U.S. Patent Number 4,359,587 which patents are specifically incorporated herein in their entirety by reference.

The starting materials are fed through a silver-containing fixed-bed catalyst installed in a vertical tubular reactor. The catalyst preferably comprises silver crystals having a particle size of from 0.1 to 3 mm, in particular from 0.2 to 2.5 mm. The fixed-bed catalyst can have a multilayer structure through arrangement of the silver crystals in layers of different particle size.

The starting mixture of methanol vapor, oxygen-containing gas, and, if used, steam and inert gas is preferably passed through the tubular reactor from top to bottom.

Otherwise, the process is carried out in one step by passing the starting mixture through the fixed catalyst bed at from 550° to 750°C., in particular from 600° to 720°C., particularly advantageously at from 660° to 700°C. The process is preferably carried out continuously at from 0.5 to 3 bar, in particular at from 0.8 to 2 bar, preferably at from 1 to 1.5 bar. The residence times in the catalyst zone are from 0.001 to 1 second, preferably from 0.002 to 0.1 second. The reaction gases leaving the catalyst zone are advantageously cooled within a short time, for example to below 350°C. The cooled gas mixture can expediently be fed to an adsorption tower, in which the formaldehyde is washed out of the gas mixture by means of water.

When methanol is used as a raw material, the reaction conditions usually fall in the following ranges:

Methanol: 1 mol percent up to 17.4 mol percent
Air: 99 mol percent to 82.6 mol percent
Reaction temperature: 350° to 600°C
Space velocity: 1,000-20,000 hr^{-1}

Preferable conditions are as follows:

Methanol: 3 mol percent to 12 mol percent
Reaction temperature: 400° to 500°C.
Space velocity: 1,000-10,000 hr^{-1}

In the present method, methamol may be used alone, or methanol and dimethyl ether can be used in admixture with each other to produce formaldehyde.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to better communicate the present invention, still another preferred aspect of the invention are depicted schematically in FIGURES 1 to 6.

Referring now to FIGURE 1, a mixture containing dimethyl ether in substantially liquid form is unloaded, for example from a road tanker (not shown), into dimethyl ether storage vessel **12** which supplies charge pump **14** through conduit **13**. Charge pump **14** transfers the liquid dimethyl ether through conduit **16** into manifold **22** which is in flow communication with an inlet of catalytic reactor **20**. Formaldehyde in dimethyl ether is supplied through conduit **18** to manifold **22**. Catalytic reactor **20** contains a catalyst which has a condensation-promoting action and is capable of hydrating dimethyl ether. Preferred catalysts are based upon a suitable molecular sieve.

It should be apparent that effluent from the catalytic reactor is a valuable product in itself. A portion of the stream can optionally be diverted from catalytic reactor **20** for delivery to a destination (not shown) where stream may subsequently be separated to recover, for example, dimethyl ether, formaldehyde, methylal and/or other polyoxymethylene dimethyl ethers. The stream can alternatively be utilized as a source of feed stock for chemical manufacturing.

The effluent stream from catalytic reactor **20** is transferred through conduits **23** and **26**, by means of pump **24**, and into ether recovery column **30**, where unreacted dimethyl ether is separated from the effluent stream to form a resulting liquid mixture of condensation products containing any unreacted formaldehyde. A dimethyl ether fraction is taken overhead through conduit **32** and into condenser **34** where a liquid condensate is formed. A suitable portion of the liquid condensate is refluxed into column **30** through conduits **35** and **36** while another portion of the condensate is supplied to manifold **22** through conduits **37** and **39**, by means of pump **38**, and into catalytic reactor **20**.

Conduit **28** supplies pump **40** with liquid from the bottom of column **30**. A suitable portion of the liquid stream from the bottom of column **30** is transferred through conduits **41** and **42**, by means of pump **40**, and into reboiler **43** which is in flow communication with the bottom of the column through conduit **44**. A liquid stream from the bottom of column **30** is transferred through conduit **45** into reactive distillation column **50**, where simultaneous chemical reaction and multicomponent distillation are carried out coextensively in the same high efficiency, continuous separation apparatus. Optionally, a stream containing methanol from storage vessel **46** may by fed into the reactive distillation column **50**. Charge pump **48** transfers methanol in substantially liquid form into the reactive distillation column **50** through conduits **47** and **49**.

Solid acidic catalyst is present in the reactive distillation column **50** to allow solutions containing water, methanol, formaldehyde, methylal and one or more other polyoxymethylene dimethyl ethers to be brought into solid-liquid contact counter-currently with the catalyst to form products including methylal and higher molecular weight polyoxymethylene dimethyl ethers. More volatile reaction products are taken overhead from the high efficiency separation apparatus, whereas water and less volatile reaction products are carried down the high efficiency separation apparatus.

The overhead vapor stream from reactive distillation column **50** is transferred through conduit **52** into condenser **54**. A suitable portion of condensate from condenser **54** is refluxed into reactive distillation column **50** through conduits **55** and **56**. A product stream containing methylal is transferred through conduit **57** to product storage (not shown). Conduit **59** supplies pump **60** with liquid containing higher molecular weight polyoxymethylene dimethyl ethers from the bottom of column **50**. A suitable portion of liquid from the bottom of column **50** is transferred, by means of pump **60**, through conduits **62** and **63** into reboiler **64** which is in flow communication with the bottom of the column by means of conduit **66**. A product stream containing higher molecular weight polyoxymethylene dimethyl ethers is transferred through conduit **68** to product storage (not shown). Preferably, an anion exchange resin is disposed within a section of the distillation column below the stages of contact with the acidic catalyst to form an essentially acid-free mixture.

An aqueous side stream containing low levels of unreacted formaldehyde and/or methanol is discharged from column **50** through conduit **58.**

In the formaldehyde preparation aspect of the invention which is described herein below, gaseous dimethyl ether is dehydrogenated in the presence of catalytically effective amount of a catalyst consisting of copper, zinc and tellurium or selenium as catalyst components. Referring now to the upper portion of FIGURE 1, a mixture containing dimethyl ether in substantially liquid form is supplied from dimethyl ether storage vessel **12** to pump **14** through conduit **13**. Dimethyl ether feedstream for formation of formaldehyde is transferred into formaldehyde reactor **90** through conduit **92**, heat exchanger **104**, and conduit **94**.

Formaldehyde reactor **90** contains particulate dehydrogenation catalyst disposed in a plurality of tubes of a vertical heat exchanger which is maintained at temperatures from about 500° to 750°C by circulation of heating fluid to the shell side of formaldehyde reactor **90** through conduit **88** from furnace **80**. Heating fluid is returned to furnace **80** through conduits **96** and **86** by means of pump **84**. Natural gas or other suitable fuel is supplied to furnace fuel manifold **82** through conduit **74** from fuel supply **72**. As described below, at least a portion of the co-product hydrogen is used as fuel for combustion with air in furnace **80**.

In this embodiment of the invention, $CuZnTeO/Al_2O_3$ or $CuZnSeO/Al_2O_3$ catalyzes the conversion of dimethyl ether to formaldehyde by a reversible dehydrogenation reaction at temperatures in a range from about 500° to 750°, preferably in a range from about 600° to 700°C:

$$CH_3OCH_3 + H_2O <--> 2CH_2O + 2H_2$$

Gaseous effluent from formaldehyde reactor **90** is transferred through conduit **102**, cooled against the reactor feedstream in exchanger **104** and then passed through conduit **106** into an adsorption tower **100** where formaldehyde and dimethyl ether are separated from a mixture of gaseous co-products including hydrogen, methane, and oxides of carbon. Adsorption tower **100** contains a high efficiency packing or other means for contacting counter-currently the gaseous stream with an adsorption liquid. Formaldehyde in methanol from the bottom of the adsorption tower is circulated in a pump-around to a lower section of the tower through conduits **112** and **116**, cooler **120**, and conduit **118** by means of pump **114**. Methanol is supplied to an upper section of the adsorption separation tower through conduit **122** by means of pump **48**. Overhead temperatures are in a range of about 15° to about 55°C, preferably about 20° to about 40°C.

A gaseous overhead stream including hydrogen, methane, and oxides of carbon is transferred through conduit **124** and into furnace fuel manifold **82** by means of blower **126**. As needed additional fuel such as natural gas is supplied to manifold **82** from a suitable fuel source **72** through conduit **74**.

As previously described, a portion of the formaldehyde in methanol solution is transferred through conduit **18** and manifold **22** into catalytic reactor **20**. Formaldehyde solution from the adsorption tower is generally from about 30 to about 85 percent by weight formaldehyde in methanol solution containing less than about 5 percent water.

Referring now to FIGURE 2, a mixture containing dimethyl ether in substantially liquid form is unloaded, for example from a road tanker (not shown), into dimethyl ether storage vessel **12** which supplies charge pump **14** through conduit **13**. Charge pump **14** transfers the liquid dimethyl ether through conduit **16** into manifold **22** which is in flow communication with an inlet of catalytic reactor **20**. Formaldehyde in dimethyl ether is supplied through conduit **18** to manifold **22**. Catalytic reactor **20** contains a catalyst which has a condensation-promoting action and is capable of hydrating dimethyl ether. Preferred catalysts are based upon a suitable molecular sieve.

It should be apparent that effluent from the catalytic reactor is a valuable product in itself. A portion of the stream can optionally be diverted from catalytic reactor **20** for delivery to a destination (not shown) where stream may subsequently be separated to recover, for example, dimethyl ether, formaldehyde, methylal and/or other polyoxymethylene dimethyl ethers. The stream can alternatively be utilized as a source of feed stock for chemical manufacturing.

The effluent stream from catalytic reactor **20** is transferred through conduits **23** and **26**, by means of pump **24**, and into ether recovery column **30**, where unreacted dimethyl ether is separated from the effluent stream to form a resulting liquid mixture of condensation products containing any unreacted formaldehyde. A dimethyl ether fraction is taken overhead through conduit **32** and into condenser **34** where a liquid condensate is formed. A suitable portion of the liquid condensate is refluxed into column **30** through conduits **35** and **36** while another portion of the condensate is supplied to manifold **22** through conduits **37** and **39**, by means of pump **38**, and into catalytic reactor **20**.

Conduit **28** supplies pump **40** with liquid from the bottom of column **30**. A suitable portion of the liquid stream from the bottom of column **30** is transferred through conduits **41** and **42**, by means of pump **40**, and into reboiler **43** which is in flow communication with the bottom of the column through conduit **44**. A liquid stream from the bottom of column **30** is transferred through conduit **45** into reactive distillation column **50**, where simultaneous chemical reaction and multicomponent distillation are carried out coextensively in the same high efficiency, continuous separation apparatus. Optionally, a stream containing methanol from storage vessel **74** may by fed into the reactive distillation column **50** through conduit **49**.

Solid acidic catalyst is present in the reactive distillation column **50** to allow solutions containing water, methanol, formaldehyde, methylal and one or more other polyoxymethylene dimethyl ethers to be brought into solid-liquid contact counter-currently with the catalyst to form products including methylal and higher molecular weight polyoxymethylene dimethyl ethers. More volatile reaction products are taken overhead from the high efficiency separation apparatus, whereas water and less volatile reaction products are carried down the high efficiency separation apparatus.

The overhead vapor stream from reactive distillation column **50** is transferred through conduit **52** into condenser **54**. A suitable portion of condensate from condenser **54** is refluxed into reactive distillation column **50** through conduits **55** and **56**. A product stream containing methylal is transferred through conduit **57** to product storage (not shown). Conduit **59** supplies pump **60** with liquid containing higher molecular weight polyoxymethylene dimethyl ethers from the bottom of column **50**. A suitable portion of liquid from the bottom of column **50** is transferred, by means of pump **60**, through conduits **62** and **63** into reboiler **64** which is in flow communication with the bottom of the column by means of conduit **66**. A product stream containing higher molecular weight polyoxymethylene dimethyl ethers is transferred through conduit **68** to product storage (not shown). Preferably, an anion exchange resin disposed within a section of the distillation column below the stages of contact with the acidic catalyst to form an essentially acid-free mixture.

An aqueous side stream containing low levels of unreacted formaldehyde and/or methanol is discharged from column **50** through conduit **58.**

The formaldehyde preparation aspect of the invention which is described herein below. In this aspect of invention, gaseous methanol is dehydrogenated in the presence of catalytically effective amount of a catalyst consisting of copper, zinc and tellurium or selenium as catalyst components. Referring now to the upper portion of FIGURE 2, a mixture containing methanol in substantially liquid form is supplied from methanol storage vessel **74** to methanol feed pump **78** through conduit **76**. Methanol feedstream is transferred through conduit **92**, preheat exchanger **104**, conduit **94**, and into formaldehyde reactor **90.**

Formaldehyde reactor **90** contains particulate dehydrogenation catalyst disposed in a plurality of tubes of a vertical heat exchanger which is maintained at temperatures from about 500° to 750°C by circulation of heating fluid to the shell side of formaldehyde reactor **90** through conduit **88** from furnace **80**. Heating fluid is returned to furnace **80** through conduits **96** and **86** by means of pump **84**. Natural gas or other suitable fuel is supplied to furnace fuel manifold **82** through conduit **81** from a suitable fuel source **83**. As described below, at least a portion of the co-product hydrogen is used as fuel for combustion with air in furnace **80**.

In this embodiment of the invention, CuZnTeO or CuZnSeO catalyzes the conversion of methanol to formaldehyde by a reversible dehydrogenation reaction at temperatures in a range from about 500° to 750°, preferably in a range from about 600° to 700°C:

$$CH_3OH <--> CH_2O + H_2$$

Gaseous effluent from formaldehyde reactor **90** is transferred through conduit **102**, cooled against the reactor feedstream in exchanger **104** and then passed through conduit **106** into a separation tower **100** where formaldehyde and methanol are separated from a mixutre of gaseous co-products including hydrogen, methane, and oxides of carbon. Adsorption tower **100** contains a high efficiency packing or other means for contacting counter-currently the gaseous stream with an adsorption liquid. Formaldehyde in methanol from the bottom of adsorption separation tower **100** is circulated in a pump-around on the adsorption tower through conduits **112** and **116**, cooler **120**, and conduit **118** by means of pump **114**. Overhead temperatures in separation tower **100** are in a range of about 15° to about 55°C, preferably about 30° to about 40°C.

As previously described, a portion of the formaldehyde in methanol solution is transferred through conduit **18** and manifold **22** into catalytic reactor **20**. Formaldehyde solution from the adsorption tower is generally from about 30 to about 85 percent by weight formaldehyde in methanol solution containing less than about 5 percent water.

A gaseous overhead stream including hydrogen, methane, and oxides of carbon is transferred through conduit **122** and into furnace fuel manifold **82** by means of blower **124**. As needed additional fuel such as natural gas is supplied to manifold **82** through conduit **81** from a suitable fuel source **83**.

Referring now to FIGURE 3, a mixture containing dimethyl ether in substantially liquid form is unloaded, for example from a road tanker (not shown), into dimethyl ether storage vessel **12** which supplies charge pump **14** through conduit **13**. Charge pump **14** transfers the liquid dimethyl ether from storage vessel **12** into catalytic reactor **20** through conduit **16** and manifold **22**. Aqueous formaldehyde in methanol is supplied to manifold **22** through conduit **18**, and into catalytic reactor **20**. Catalytic reactor **20** contains a catalyst which has a condensation-promoting action and is capable of hydrating dimethyl ether. Preferred catalysts are based upon a suitable molecular sieve.

It should be apparent that effluent from the catalytic reactor is a valuable product in itself. A portion of the stream can optionally be diverted from catalytic reactor **20** for delivery to a destination (not shown) where stream may subsequently be separated to recover, for example, dimethyl ether, formaldehyde, methylal and/or other polyoxymethylene dimethyl ethers. The stream can alternatively be utilized as a source of feed stock for chemical manufacturing.

The effluent stream from catalytic reactor **20** is transferred through conduits **23** and **26**, by means of pump **24**, and into ether recovery column **30**, where unreacted dimethyl ether is separated from the effluent stream to form a resulting liquid mixture of condensation products containing any unreacted formaldehyde. A dimethyl ether fraction is taken overhead through conduit **32** and into condenser **34** where a liquid condensate is formed. A suitable portion of the liquid condensate is refluxed into column **30** through conduits **35** and **36** while another portion of the condensate is supplied to manifold **22** through conduits **37** and **39**, by means of pump **38**, and into catalytic reactor **20**.

Conduit **28** supplies pump **40** with liquid from the bottom of column **30**. A suitable portion of the liquid stream from the bottom of column **30** is transferred through conduits **41** and **42**, by means of pump **40**, and into reboiler **43** which is in flow communication with the bottom of the column through conduit **44**. A liquid stream from the bottom of column **30** is transferred through conduit **45** into reactive distillation column **50**, where simultaneous chemical reaction and multicomponent distillation are carried out coextensively in the same high efficiency, continuous separation apparatus. Optionally, a stream containing methanol from storage vessel **46** may by fed into the reactive distillation column **50**. Charge pump **48** transfers methanol in substantially liquid form into the reactive distillation column **50** through conduits **47** and **49**.

Solid acidic catalyst is present in the reactive distillation column **50** to allow solutions containing water, methanol, formaldehyde, methylal and one or more other polyoxymethylene dimethyl ethers to be brought into solid-liquid contact counter-currently with the catalyst to form products including methylal and higher molecular weight polyoxymethylene dimethyl ethers. More volatile reaction products are taken overhead from the high efficiency separation apparatus, whereas water and less volatile reaction products are carried down the high efficiency separation apparatus.

The overhead vapor stream from reactive distillation column **50** is transferred through conduit **52** into condenser **54**. A suitable portion of condensate from condenser **54** is refluxed into reactive distillation column **50** through conduits **55** and **56**. A product stream containing methylal is transferred through conduit **58** to product storage (not shown). Conduit **59** supplies pump **60** with liquid containing higher molecular weight polyoxymethylene dimethyl ethers from the bottom of column **50**. A suitable portion of liquid from the bottom of column **50** is transferred, by means of pump **60**, through conduits **62** and **63** into reboiler **64** which is in flow communication with the bottom of the column by means of conduit **66**. A product stream containing higher molecular weight polyoxymethylene dimethyl ethers is transferred through conduit **68** to product storage (not shown). Preferably, an anion exchange resin disposed within a section of the distillation column below the stages of contact with the acidic catalyst to form an essentially acid-free mixture.

An aqueous side stream containing low levels of unreacted formaldehyde and/or methanol is discharged from column **50** through conduit **72.** The side stream from column **50** is transferred by means of pump **74** through conduit **75** to waste disposal (not shown).

In the formaldehyde preparation aspect of the invention which is described herein below, a gaseous feedstream comprising dimethyl ether, dioxygen and diluent is contacted with a catalytically effective amount of an oxidation promoting catalyst comprising tungsten oxide as an essential catalyst component. In this embodiment of invention, recycle gas from the formaldehyde absorber is combined with air, mixed with dimethyl ether, preheated against reactor product, and then fed to the formaldehyde reactor.

Referring now to the upper portion of FIGURE 3, a mixture containing dimethyl ether in substantially liquid form is supplied from dimethyl ether storage vessel **12** to pump **14** through conduit **13**, and into feed manifold **92** through conduit **15**. By means of blower **78** a recycle stream of wet gas is transferred into feed manifold **92** through conduit **98**. A gaseous stream containing dioxygen and dinitrogen from a source (not shown) is supplied to compressor **94** through conduit **93**. Compressed gas is transferred through conduit **95**, combined in feed manifold **92** with the recycle stream of wet gas from the formaldehyde adsorber and the dimethyl ether. The resulting feed mixture is heated against reactor effluent in heat exchanger **76**, and transferred into oxidation reactor **90** through conduit **91**.

The mole ratio of fresh air feed to dimethyl ether is about 3.5, and the mole ratio of recycled gas to fresh air feed is about 2.1. Oxidation reactor **90** is a vertical heat exchanger. The tubes are filled with catalyst pellets. (The upper and lower regions of the tubes contain pellets of inert material.) Typically, a portion of heat generated in the catalyst bed is diverted to steam generation within oxidation reactor **90** thereby providing cooling of effluent from the bed (not shown). A thermal fluid is vaporized on the shell side and circulated to a steam generator to generate steam at pressures of up to 300 psig.

Within the oxidation reaction zone of reactor **90** is an oxidation-promoting catalyst, preferably consisting essentially of a metal oxide component with or without a supplemental inorganic compound. In a preferred embodiment on this invention, tungsten oxide catalysts are used because they give almost complete oxidation to formaldehyde at much lower temperatures than are required for the silver-catalyzed dehydrogenation reaction.

In this embodiment of the invention, tungsten oxide catalyzes the conversion of dimethyl ether to formaldehyde by an oxidation reaction at temperatures in a range from about 350° to about 600°C , preferably in a range from about 400° to about 500°C:

$$CH_3OCH_3 + O_2 \dashrightarrow 2CH_2O + H_2O$$

In this case, a large excess of air is necessary to obtain maximum yields and to avoid explosive feed concentrations. Some flexibility exists in the explosive limits, depending upon the temperature, pressure, and normal moisture content of the air. However, normal practical limitations appear to set a lower boundary between 8 mol percent and 10 mol percent in the reactor feed.

Several side reactions occur, especially those producing carbon monoxide, formic acid, and dimethyl ether. However, because of a lower reaction temperature, the extent of these reactions is smaller than in the silver-catalyzed process.

Gaseous effluent from oxidation reactor **90** is transferred through conduit **96**, cooled against the reactor feedstream in exchanger **76** and then passed through conduit **97** into spray column **100** where a solution of aqueous formaldehyde in methanol is formed. Formaldehyde solution from the bottom of spray column **100**, at temperatures in a range downward from about 100°C to about 75°C, is supplied to pump **104** through conduit **103**. As previously described, a portion of the aqueous formaldehyde in methanol is transferred through conduit **18** and manifold **22** into catalytic reactor **20**. Formaldehyde solution from the spray column is generally from about 30 to about 85 percent by weight formaldehyde in methanol solution containing less than about 5 percent water and less than 350 ppm of formic acid. Another portion of the aqueous formaldehyde solution is combined with a crude solution of formaldehyde in methanol, supplied from the bottom adsorption column **110** through conduits **113** and **108**, by means of pump **114**. The combination forms a stream which is circulated to the top of spray column **100** through conduit **106**. It is important to maintain the temperature of the pump-around stream above about 70°C to prevent paraformaldehyde formation. Optionally, a portion of the cooling required in spray column **100** may be obtained by including a heat exchanger in the flow through conduit **106**.

A gaseous overhead stream from spray column **100** is transferred through conduit **102** into adsorption column **110**, which contains a high efficiency packing or other means for contacting counter-currently the gaseous stream with aqueous adsorption liquid. A crude solution of formaldehyde in methanol from the bottom of adsorption column **110** is circulated in a pump-around to a lower section of the column through conduits **113** and **115**, cooler **116**, and conduit **117** by means of pump **114**.

As needed, methanol for the adsorption is supplied to a section of adsorption column **110** by means of pump **48** through conduit **125**, cooler **126**, and conduit **128**. Further up the column, pump-arounds may be cooled to successively lower temperatures. In some configurations, the lower pump-around stream is not cooled at all.

A vapor side draw from adsorption column **110** is transferred through conduit **112** and mixed with fresh air as previously described. The adsorber overhead passes through conduit **118** into condenser **122**. An appropriate amount of condensate is formed and refluxed to the top section of the adsorber column through conduit **124**. Overhead temperatures in adsorption column **110** are in a range of about 15° to about 55°C, preferably about 30° to about 40°C. Gases are vented from condenser **122** through conduit **120** to disposal, typically, in a thermal oxidation unit (not shown).

Referring now to FIGURE 4, a mixture containing dimethyl ether in substantially liquid form is unloaded, for example from a road tanker (not shown), into dimethyl ether storage vessel **12** which supplies charge pump **14** through conduit **13**. Charge pump **14** transfers the liquid dimethyl ether from storage vessel **12** into catalytic reactor **20** through conduit **16** and manifold **22**. Aqueous formaldehyde is supplied to manifold **22** through conduit **18**, and into catalytic reactor **20** which contains a condensation-promoting catalyst based upon a suitable molecular sieve.

It should be apparent that effluent from the catalytic reactor is a valuable product in itself. A portion of the stream can optionally be diverted from catalytic reactor **20** for delivery to a destination (not shown) where stream may subsequently be separated to recover, for example, dimethyl ether, formaldehyde, methylal and/or other polyoxymethylene dimethyl ethers. The stream can alternatively be utilized as a source of feed stock for chemical manufacturing.

The effluent stream from catalytic reactor **20** is transferred through conduits **23** and **26**, by means of pump **24**, and into ether recovery column **30**, where unreacted dimethyl ether is separated from the effluent stream to form a resulting liquid mixture of condensation products containing any unreacted formaldehyde. A dimethyl ether fraction is taken overhead through conduit **32** and into condenser **34** where a liquid condensate is formed. A suitable portion of the liquid condensate is refluxed into column **30** through conduits **35** and **36** while another portion of the condensate is supplied to manifold **22** through conduits **37** and **39**, by means of pump **38**, and into catalytic reactor **20**.

Conduit **28** supplies pump **40** with liquid from the bottom of column **30**. A suitable portion of the liquid stream from the bottom of column **30** is transferred through conduits **41** and **42**, by means of pump **40**, and into reboiler **43** which is in flow communication with the bottom of the column through conduit **44**. A liquid stream from the bottom of column **30** is transferred through conduit **45** into reactive distillation column **50**, where simultaneous chemical reaction and multicomponent distillation are carried out coextensively in the same high efficiency, continuous separation apparatus. Optionally, a stream containing methanol from storage vessel **46** may by fed into the reactive distillation column **50**. Charge pump **48** transfers methanol in substantially liquid form into the reactive distillation column **50** through conduits **47** and **49**.

Solid acidic catalyst is present in the reactive distillation column **50** to allow solutions containing water, methanol, formaldehyde, methylal and one or more other polyoxymethylene dimethyl ethers to be brought into solid-liquid contact counter-currently with the catalyst to form products including methylal and higher molecular weight polyoxymethylene dimethyl ethers. More volatile reaction products are taken overhead from the high efficiency separation apparatus, whereas water and less volatile reaction products are carried down the high efficiency separation apparatus.

The overhead vapor stream from reactive distillation column **50** is transferred through conduit **52** into condenser **54**. A suitable portion of condensate from condenser **54** is refluxed into reactive distillation column **50** through conduits **55** and **56**. A product stream containing methylal is transferred through conduit **58** to product storage (not shown). Conduit **59** supplies pump **60** with liquid containing higher molecular weight polyoxymethylene dimethyl ethers from the bottom of column **50**. A suitable portion of liquid from the bottom of column **50** is transferred, by means of pump **60**, through conduits **62** and **63** into reboiler **64** which is in flow communication with the bottom of the column by means of conduit **66**. A product stream containing higher molecular weight polyoxymethylene dimethyl ethers is transferred through conduit **68** to product storage (not shown). Preferably, an anion exchange resin is disposed within a section of the distillation column below the stages of contact with the acidic catalyst to form an essentially acid-free mixture.

An aqueous side stream containing low levels of unreacted formaldehyde and/or methanol is discharged from column **50** through conduit **72.**

In this aspect of invention, recycle gas from the formaldehyde absorber is combined with air, mixed with dimethyl ether, preheated against reactor product, and then fed to the formaldehyde reactor.

Referring now to the upper portion of FIGURE 4, a mixture containing dimethyl ether in substantially liquid form is supplied from dimethyl ether storage vessel **12** to pump **14** through conduit **13**. Dimethyl ether is transferred through conduit **15** into feed manifold **92**. A recycle stream of wet gas is transferred into feed manifold **92** by means of blower **88**. A gaseous stream containing dioxygen and dinitrogen from a source (not shown) is supplied to compressor **94** through conduit **93**. Compressed gas is transferred through conduit **95**, combined in feed manifold **92** with the recycle stream of wet gas from the formaldehyde adsorber and the dimethyl ether. The resulting mixture is heated against reactor effluent in heat exchanger **80**, and transferred into oxidation reactor **90** through conduit **82** and feed manifold **84**

Formaldehyde reactor **90** contains an oxidative dehydrogenation catalyst disposed in thin layer directly above a vertical heat exchanger where effluent from the catalyst layer is promptly cooled. Boiler feed water at about 110° to 130°C is supplied through conduit **85** to the heat exchanger for generation of low pressure steam in the lower section of the formaldehyde reactor. The steam is transferred through conduit **86**, mixed with the preheated mixture of dimethyl ether, wet recycle gas and air stream in feed manifold **84**, and transferred into formaldehyde reactor **90**. Steam is metered into the preheated methanol-air mixture to control the reactor outlet temperature. The mole ratio of fresh air feed to methanol is between 0.5 and 2.0, preferably about 1.25 and typically the mole ratio of dimethyl ether to steam is about 3. The pressure is only slightly above atmospheric. Since the catalyst layers are less than one inch in thickness, the pressure drop is negligible.

In this embodiment of the invention, metallic silver catalyzes the conversion of dimethyl ether to formaldehyde by a reversible dehydrogenation reaction at temperatures from about 500° to 700°C:

$$CH_3OCH_3 + 1/2\ O_2 \dashrightarrow 2CH_2O + H_2$$

The oxidative dehydrogenation catalyst is generally silver crystals supported on a stainless steel mesh, or a shallow bed of silver crystals, spherical particles, or granules. The reaction is endothermic, and theoretical equilibrium is approximately 50 percent yield at 400°C, 90 percent at 500°C, and 99 percent at 700°C. To conveniently sustain elevated reaction temperatures required to obtain high yields, a portion of the hydrogen formed is oxidized to water. Formation of water is exothermic and provides heat to maintain the endothermic hydrogenation reaction. Heat is also provided by the direct oxidation of methanol:

$$CH_3OH + 1/2\ O_2 \dashrightarrow CH_2O + H_2O$$

These reactions are rapid and therefore the process is essentially adiabatic. At 650°C, the reaction is substantially complete with contact times of less than 0.01 second. Methanol conversion in the reactor is typically between 65 percent and 80 percent, depending largely on the amount of steam introduced at the methanol vaporization step. Formaldehyde is lost by several side reactions, including those producing co-products including carbon monoxide, carbon dioxide, methane, formic acid, and methyl formate.

To minimize side reactions, it is important to avoid excess oxygen and to operate with exposure time of products and reactants to the catalyst at high temperatures as short as possible. An excess of methanol or methanol and steam is also important, serving to avoid an explosive feed composition. A mixture containing between 6.7 mol percent and 36.5 mol percent methanol in air at 1 atm constitutes a severe explosion hazard.

Gaseous effluent from oxidation reactor **90** is transferred through conduit **96**, cooled against the reactor feedstream in exchanger **80** and then passed to an absorption system, where methanol and formaldehyde are absorbed. The effluent gases flow through conduit **98** into spray column **100** where a solution of formaldehyde is formed. Formaldehyde solution from the bottom of spray column **100**, at temperatures in a range downward from about 100°C to about 75°C, is supplied to pump **104** through conduit **103**. As previously described, a portion of the aqueous formaldehyde is transferred through conduit **18** and manifold **22** into catalytic reactor **20**. Formaldehyde solution from the spray column is generally about 55 percent by weight formaldehyde, about 43 methanol weight percent about 2 weight percent water and less than 350 ppm of formic acid. Another portion of the formaldehyde solution is combined with crude formalin solution, supplied from the bottom adsorption column **110** through conduits **113** and **108**, by means of pump **114**, and circulated to the top of spray column **100** through conduit **106**. It is important to maintain the temperature of the pump-around stream above about 70°C to prevent paraformaldehyde formation. Optionally, a portion of the cooling required in spray column **100** may be obtained by including a heat exchanger in the flow through conduit **106**.

A gaseous overhead stream from spray column **100** is transferred through conduit **102** into adsorption column **110**, which contains a high efficiency packing or other means for contacting counter-currently the gaseous stream with aqueous adsorption liquid. A dilute aqueous formaldehyde from the bottom of adsorption column **110** is circulated in a pump-around to the bottom section of the column through conduits **113** and **115**, cooler **116**, and conduit **117** by means of pump **114**.

Further up the column pump-arounds are be cooled to successively lower temperatures. In this embodiment of the invention a liquid side stream is supplied to pump **124** through conduit **125**, transferred through manifold **127**, cooled in cooler **126**, and returned to adsorption column **110** through conduit **128**.

In some configurations, the lower pump-around stream is not cooled at all. Caustic solution may be added to the chilled water to improve absorber performance, but it leaves traces of sodium as a contaminant in the product.

A vapor side draw from adsorption column **110** is transferred through conduit **112** and mixed with fresh air as previously described.

The adsorber overhead passes through conduit **118** into condenser **122**. An appropriate amount of condensate is formed and refluxed to the top section of the adsorber column through conduit **123**. Overhead temperatures in adsorption column **110** are in a range of about 15° to about 55°C, preferably about 30° to about 40°C. Gases are vented from condenser **122** through conduit **120** to disposal, typically, in a thermal oxidation unit (not shown).

The absorber overhead, which contains trace amounts of formaldehyde (about 10-30 ppm), is treated in several ways by catalytic or thermal converter to oxidize hydrocarbons and recuperative heat exchange. Typically, 170 psig to 200 psig steam is generated to improve overall economics of preferred embodiments of the invention.

Referring now to FIGURE 5, a mixture containing dimethyl ether in substantially liquid form is unloaded, for example from a road tanker (not shown), into dimethyl ether storage vessel **12** which supplies charge pump **14** through conduit **13**. Charge pump **14** transfers the liquid dimethyl ether from storage vessel **12** into catalytic reactor **20** through conduit **16** and manifold **22**. Aqueous formaldehyde is supplied to manifold **22** through conduit **18**, and into catalytic reactor **20** which contains a condensation-promoting catalyst based upon a suitable molecular sieve.

It should be apparent that effluent from the catalytic reactor is a valuable product in itself. A portion of the stream can optionally be diverted from catalytic reactor **20** for delivery to a destination (not shown) where stream may subsequently be separated to recover, for example, dimethyl ether, formaldehyde, methylal and/or other polyoxymethylene dimethyl ethers. The stream can alternatively be utilized as a source of feed stock for chemical manufacturing.

The effluent stream from catalytic reactor **20** is transferred through conduits **23** and **26**, by means of pump **24**, and into ether recovery column **30**, where unreacted dimethyl ether is separated from the effluent stream to form a resulting liquid mixture of condensation products containing any unreacted formaldehyde. A dimethyl ether fraction is taken overhead through conduit **32** and into condenser **34** where a liquid condensate is formed. A suitable portion of the liquid condensate is refluxed into column **30** through conduits **35** and **36** while another portion of the condensate is supplied to manifold **22** through conduits **37** and **39**, by means of pump **38**, and into catalytic reactor **20**.

Conduit **28** supplies pump **40** with liquid from the bottom of column **30**. A suitable portion of the liquid stream from the bottom of column **30** is transferred through conduits **41** and **42**, by means of pump **40**, and into reboiler **43** which is in flow communication with the bottom of the column through conduit

44. A liquid stream from the bottom of column **30** is transferred through conduit **45** into reactive distillation column **50**, where simultaneous chemical reaction and multicomponent distillation are carried out coextensively in the same high efficiency, continuous separation apparatus. Optionally, a stream containing methanol may by fed into the reactive distillation column **50** through conduit **49**.

Solid acidic catalyst is present in the reactive distillation column **50** to allow solutions containing water, methanol, formaldehyde, methylal and one or more other polyoxymethylene dimethyl ethers to be brought into solid-liquid contact counter-currently with the catalyst to form products including methylal and higher molecular weight polyoxymethylene dimethyl ethers. More volatile reaction products are taken overhead from the high efficiency separation apparatus, whereas water and less volatile reaction products are carried down the high efficiency separation apparatus.

The overhead vapor stream from reactive distillation column **50** is transferred through conduit **52** into condenser **54**. A suitable portion of condensate from condenser **54** is refluxed into reactive distillation column **50** through conduits **55** and **56**. A product stream containing methylal is transferred through conduit **58** to product storage (not shown). Conduit **59** supplies pump **60** with liquid containing higher molecular weight polyoxymethylene dimethyl ethers from the bottom of column **50**. A suitable portion of liquid from the bottom of column **50** is transferred, by means of pump **60**, through conduits **62** and **63** into reboiler **64** which is in flow communication with the bottom of the column by means of conduit **66**. A product stream containing higher molecular weight polyoxymethylene dimethyl ethers is transferred through conduit **68** to product (not shown). Preferably, an anion exchange resin disposed within a section of the distillation column below the stages of contact with the acidic catalyst to form an essentially acid-free mixture.

An aqueous side stream containing low levels of unreacted formaldehyde and/or methanol is discharged from column **50** through conduit **72.** A portion of the side stream from column **50** is supplied by means of pump **74** through conduit **75** for use as makeup water in the formaldehyde adsorption aspect of the invention which is described herein below.

In this aspect of invention, recycle gas from the formaldehyde absorber is combined with air, mixed with methanol which is preheated against reactor product, and then fed to the formaldehyde reactor.

Referring now to the upper portion of FIGURE 5, a mixture containing methanol in substantially liquid form is supplied from methanol storage vessel **86** to methanol feed pump **88** through conduit **87**. Methanol is transferred through conduit **89**, heat exchanger **76**, conduit **91**, feed manifold **92** and into oxidation reactor **90**. A recycle stream of wet gas is transferred into oxidation reactor **90** through conduit **98** and manifold **92** by means of blower **78**. A gaseous stream containing dioxygen and dinitrogen from a source (not shown) is supplied to compressor **94** through conduit **93**. Compressed gas is transferred through conduit **95**, combined in conduit **98** with a recycle stream of wet gas from the formaldehyde adsorber through conduit **112** and transferred into oxidation reactor **90** through manifold **92** by means of blower **78**.

The mole ratio of fresh air feed to methanol is about 3.5, and the mole ratio of recycled gas to fresh air feed is about 2.1. Oxidation reactor **90** is a vertical heat exchanger. The tubes are filled with catalyst pellets. (The upper and lower regions of the tubes contain pellets of inert material.) Typically, a portion of heat generated in the catalyst bed is diverted to steam generation within oxidation reactor **90** thereby providing cooling of effluent from the bed (not shown). A thermal fluid is vaporized on the shell side and circulated to a steam generator to generate steam at pressures of up to 300 psig.

Within the oxidation reaction zone of reactor **90** is an oxidation-promoting catalyst, preferably consisting essentially of a metal oxide component with or without a supplemental inorganic compound. In a preferred embodiment on this invention, ferric molybdate catalysts are used because they give almost complete oxidation to formaldehyde at much lower temperatures than are required for the silver-catalyzed dehydrogenation reaction.

In this embodiment of the invention, ferric molybdate catalyzes the conversion of methanol to formaldehyde by an oxidation reaction at 320° to 370°C:

$$CH_3OH + 1/2\, O_2 \dashrightarrow CH_2O + H_2O$$

In this case, a large excess of air is necessary to obtain maximum yields and to avoid explosive feed concentrations. Some flexibility exists in the explosive limits, depending upon the temperature, pressure, and normal moisture content of the air. However, normal practical limitations appear to set a lower boundary between 8 mol percent and 10 mol percent in the reactor feed.

Several side reactions occur, especially those producing carbon monoxide, formic acid, and dimethyl ether. However, because of a lower reaction temperature, the extent of these reactions is smaller than in the silver-catalyzed process.

Gaseous effluent from oxidation reactor **90** is transferred through conduit **96**, cooled against vaporizing feed methanol in exchanger **76** and then passed to an absorption system, where methanol and formaldehyde are absorbed in water. The effluent gases flow through conduit **97** into spray column **100** where an aqueous solution of formaldehyde is formed. Aqueous formaldehyde solution from the bottom of spray column **100**, at temperatures in a range downward from about 100°C to about 75°C, is supplied to pump **104** through conduit **103**. As previously described, a portion of the aqueous formaldehyde is transferred through conduit **18** and manifold **22** into catalytic reactor **20**. Aqueous formaldehyde from the spray column is generally about 50 percent by weight formaldehyde containing less than 0.5 weight percent methanol and less than 350 ppm of formic acid. Another portion of the aqueous formaldehyde solution is combined with crude formalin solution, supplied from the bottom of adsorption column **110** through conduits **113** and **108**, by means of pump **114**, and circulated to the top of spray column **100** through conduit **106**. It is important to maintain the temperature of the pump-around stream above about 70°C to prevent paraformaldehyde formation. Optionally, a portion of the cooling required in spray column **100** may be obtained by including a heat exchanger in the flow through conduit **106**.

A gaseous overhead stream from spray column **100** is transferred through conduit **102** into adsorption column **110**, which contains a high efficiency packing or other means for contacting counter-currently the gaseous stream with aqueous adsorption liquid. A dilute aqueous formaldehyde from the bottom of adsorption column **110** is circulated in a pump-around to the bottom section of the column through conduits **113** and **115**, cooler **116**, and conduit **117** by means of pump **114**.

As needed, makeup water for the adsorption is supplied to an upper section of adsorption column **110** from column **50** by means of pump **74** through conduit **75**, cooler **126**, and conduit **128**. Further up the column, pump-arounds may be cooled to successively lower temperatures. In some configurations, the lower pump-around stream is not cooled at all. Caustic solution may be added to the chilled water to improve absorber performance, but it leaves traces of sodium as a contaminant in the product.

A vapor side draw from adsorption column **110** is transferred through conduit **112** and mixed with fresh air as previously described. The adsorber overhead passes through conduit **118** into condenser **122**. An appropriate amount of condensate is formed and refluxed to the top section of the adsorber column through conduit **124**. Temperatures in adsorption column **110** are in a range of about 15° to about 55°C, preferably about 30° to about 40°C. Gases are vented from condenser **122** through conduit **120** to disposal, typically, in a thermal oxidation unit (not shown).

Referring now to FIGURE 6, a mixture containing dimethyl ether in substantially liquid form is unloaded, for example from a road tanker (not shown), into dimethyl ether storage vessel **12** which supplies charge pump **14** through conduit **13**. Charge pump **14** transfers the liquid dimethyl ether from storage vessel **12** into catalytic reactor **20** through conduit **16** and manifold **22**. Aqueous formaldehyde is supplied to manifold **22** through conduit **18**, and into catalytic reactor **20** which contains a condensation-promoting catalyst based upon a suitable molecular sieve.

It should be apparent that effluent from the catalytic reactor is a valuable product in itself. A portion of the stream can optionally be diverted from catalytic reactor **20** for delivery to a destination (not shown) where stream may subsequently be separated to recover, for example, dimethyl ether, formaldehyde, methylal and/or other polyoxymethylene dimethyl ethers. The stream can alternatively be utilized as a source of feed stock for chemical manufacturing.

The effluent stream from catalytic reactor **20** is transferred through conduits **23** and **26**, by means of pump **24**, and into ether recovery column **30**, where unreacted dimethyl ether is separated from the effluent stream to form a resulting liquid mixture of condensation products containing any unreacted formaldehyde. A dimethyl ether fraction is taken overhead through conduit **32** and into condenser **34** where a liquid condensate is formed. A suitable portion of the liquid condensate is refluxed into column **30** through conduits **35** and **36** while another portion of the condensate is supplied to manifold **22** through conduits **37** and **39**, by means of pump **38**, and into catalytic reactor **20**.

Conduit **28** supplies pump **40** with liquid from the bottom of column **30**. A suitable portion of the liquid stream from the bottom of column **30** is transferred through conduits **41** and **42**, by means of pump **40**, and into reboiler **43** which is in flow communication with the bottom of the column through conduit **44**. A liquid stream from the bottom of column **30** is transferred through conduit **45** into reactive distillation column **50**, where simultaneous chemical reaction and multicomponent distillation are carried out coextensively in the same high efficiency, continuous separation apparatus. Optionally, a stream containing methanol may by fed into the reactive distillation column **50**.

Solid acidic catalyst is present in the reactive distillation column **50** to allow solutions containing water, methanol, formaldehyde, methylal and one or more other polyoxymethylene dimethyl ethers to be brought into solid-liquid contact counter-currently with the catalyst to form products including methylal and higher molecular weight polyoxymethylene dimethyl ethers. More volatile reaction products are taken overhead from the high efficiency separation apparatus, whereas water and less volatile reaction products are carried down the high efficiency separation apparatus.

The overhead vapor stream from reactive distillation column **50** is transferred through conduit **52** into condenser **54**. A suitable portion of condensate from condenser **54** is refluxed into reactive distillation column **50** through conduits **55** and **56**. A product stream containing methylal is transferred through conduit **58** to product storage (not shown). Conduit **59** supplies pump **60** with liquid containing higher molecular weight polyoxymethylene dimethyl ethers from the bottom of column **50**. A suitable portion of liquid from the bottom of column **50** is transferred, by means of pump **60**, through conduits **62** and **63** into reboiler **64** which is in flow communication with the bottom of the column by means of conduit **66**. A product stream containing higher molecular weight polyoxymethylene dimethyl ethers is transferred through conduit **68** to product storage (not shown). Preferably, an anion exchange resin disposed within a section of the distillation column below the stages of contact with the acidic catalyst to form an essentially acid-free mixture.

An aqueous side stream containing low levels of unreacted formaldehyde and/or methanol is discharged from column **50** through conduit **72.** A portion of the side stream from column **50** is supplied by means of pump **74** through conduit **75** for use as makeup water in the formaldehyde adsorption aspect of the invention which is described herein below.

In this aspect of invention, methanol is vaporized into a stream of air which is preheated against reactor product, mixed with steam, and then fed into the formaldehyde reactor.

The silver-catalyzed process dehydrogenates methanol to formaldehyde. The reaction is endothermic, but the addition of oxygen (usually as air) oxidizes co-product hydrogen to water in a strongly exothermic reaction to maintain the overall reaction at a temperature of about 590-620°'C.

Referring now to the upper portion of FIGURE 6, a mixture containing methanol in substantially liquid form is supplied from methanol storage vessel **86** to methanol feed pump **88** through conduit **87**. Methanol is transferred through conduit **89** into methanol vaporizer **90**.

Air or other gaseous stream containing dioxygen and dinitrogen from a source (not shown) is supplied to methanol vaporizer **90** by means of blower **94** through conduits **93** and **95**. Liquid methanol from the bottom of vaporizer **90** is circulated by means of pump **76** in a pump-around through conduits **96** and **97**, heater **78**, and conduit **98**. This allows the vaporization of methanol to be carried out at temperatures in a range from about 40° to about 80°C, preferably from about 45° to about 60°C.

A gaseous stream is transferred from the vaporizer through conduit **92**, preheat exchanger **108**, conduit **102**, feed manifold **103** and into formaldehyde reactor **100**, which contains an oxy-dehydrogenation catalyst disposed in thin layer directly above a vertical heat exchanger where effluent from the catalyst layer is promptly cooled. Boiler feed water at about 110° to 130°C is supplied through conduit **91** to the heat exchanger for generation of low pressure steam in the lower section of the formaldehyde reactor. The steam is transferred through conduit **104**, mixed with the preheated methanol and air stream in feed manifold **103** and into formaldehyde reactor **100**. Steam is metered into the preheated methanol-air mixture to control the reactor outlet temperature. The mole ratio of fresh air feed to methanol is between 0.5 and 2.0, preferably about 1.25 and typically the mole ratio of methanol to steam is about 3. The pressure is only slightly above atmospheric. Since the catalyst layers are less than one inch in thickness, the pressure drop is negligible.

In this embodiment of the invention, metallic silver catalyzes the conversion of methanol to formaldehyde by a reversible dehydrogenation reaction at temperatures from about 500° to 700°C:

$$CH_3OH \dashrightarrow CH_2O + H_2$$

The oxy-dehydrogenation catalyst is generally silver crystals supported on a stainless steel mesh or other suitable support such as alumina. Such catalysts are disposed as a shallow bed of silver crystals, spherical particles, or granules. The reaction is endothermic, and theoretical equilibrium is approximately 50 percent yield at 400°C, 90 percent at 500°C, and 99 percent at 700°C. To conveniently sustain elevated reaction temperatures required to obtain high yields, a portion of the hydrogen formed is oxidized to water. Formation of water is exothermic and provides heat to maintain the endothermic hydrogenation reaction. Heat is also provided by the direct oxidation of methanol:

$$CH_3OH + 1/2\,O_2 \dashrightarrow CH_2O + H_2O$$

These reactions are rapid and therefore the process is essentially adiabatic. At 650°C, the reaction is substantially complete with contact times of less than 0.01 second. Methanol conversion in the reactor is typically between 65 percent and 80 percent, depending largely on the amount of steam introduced at the methanol vaporization step. Formaldehyde is lost by several side reactions, including those producing co-products including carbon monoxide, carbon dioxide, methane, formic acid, and methyl formate.

To minimize side reactions, it is important to avoid excess oxygen and to operate with exposure time of products and reactants to the catalyst at high temperatures as short as possible. An excess of methanol or methanol and steam is also important, serving to avoid an explosive feed composition. A mixture containing between 6.7 mol percent and 36.5 mol percent methanol in air at 1 atm constitutes a severe explosion hazard.

Gaseous effluent from oxidation reactor **100** is transferred through conduit **106**, further cooled by heat exchange against the gaseous feed stream of methanol and air to just above their dew point in exchanger **108** and then passed through conduit **112** into an absorption column **110**, where methanol and formaldehyde are absorbed in water.

Adsorption column **110** operating at approximately atmospheric pressure contains a high efficiency packing or other means for contacting counter-currently the gaseous stream with aqueous adsorption liquids. For example, the adsorption column may be provided with packing in the lower two sections of the absorber and an upper section may contain about ten valve trays. Aqueous formaldehyde from the bottom of adsorption column **110** is circulated in a pump-around to the bottom section of the column through conduits **113** and **115**, cooler **116**, and conduit **117** by means of pump **114**. Further up the column, optionally pump-arounds may be used which are cooled to successively lower temperatures. It is important to maintain the temperature of the lower pump-around stream above about 70°C to prevent paraformaldehyde formation. In some configurations, the lower pump-around stream is not cooled at all.

Aqueous formaldehyde from the bottom of adsorption column **110** is generally about 40 to 45 percent by weight formaldehyde containing about 10 to 15 weight percent methanol and less than 250 ppm of formic acid. As previously described, a portion of the aqueous formaldehyde is transferred through conduit **18** and manifold **22** into catalytic reactor **20**.

Makeup water for the adsorption is supplied to an upper section of adsorption column **110** from column **50** by means of pump **74** through conduit **75**, cooler **126**, and conduit **128**.

The adsorber overhead passes through conduit **118** into condenser **122**. An appropriate amount of condensate is formed and refluxed to the top section of the adsorber column through conduit **124**. Overhead temperatures in adsorption column **110** are in a range of about 5° to about 15°C, preferably about 10°C Gases are vented from condenser **122** through conduit **120** to disposal, typically, in a thermal oxidation unit (not shown).

The absorber overhead, which contains trace amounts of formaldehyde (about 10-30 ppm), is treated in several ways by catalytic or thermal converter to oxidize hydrocarbons and recuperative heat exchange. Typically, 170 psig to 200 psig steam is generated to improve overall economics of preferred embodiments of the invention.

In view of the features and advantages of the continuous catalytic processes for direct condensation of formaldehyde and dimethyl ether to form a mixture containing one or more polyoxymethylene dimethyl ethers in accordance with this invention, as compared to the known methanol condensation systems previously used, the following examples are given.

EXAMPLES 1 to 3

In Examples 1, 2 and 3 a crystalline borosilicate catalyst exhibiting the MFI crystal structure was used to convert a predominately dimethyl ether feedstream and a liquid feedstream of aqueous formaldehyde in methanol. Effluent of the condensation reactor comprised water, methanol, formaldehyde, dimethyl ether, methylal and higher polyoxymethylene dimethyl ethers having a structure represented by the type formula

$$CH_3O(CH_2O)_nCH_3$$

in which formula n is a number from 1 to about 7.

Crystalline borosilicate molecular sieve in the form of an extrudate (1/16 inch) was calcined overnight at 500° C. The calcined extrudate was crushed and sieved to 18-40 mesh. A tubular quartz reactor was charged with 3.27 grams (5 cc) of the sieved particles. The tubular quartz reactor (approx. 10 mm inside diameter) was equipped with a quartz thermowell terminating at about the midpoint of the catalyst bed.

A liquid feed solution was prepared in a pressurized 50 mL autoclave using 11.13 grams of paraformaldehyde (95%), 15.94 grams of methanol, and 1.80 grams of water. Contents of the autoclave were stirred and heated to temperatures of 130° to 140° C for 1 hour, and then cooled. The resulting solution was fed by a syringe pump into a preheat zone above the catalyst bed. Using mass flow controllers, a gas feed mixture of dimethyl ether and nitrogen was also fed to the top of the reactor.

Liquid products from the reactor were collected in a cool (0°C) 25 mL flask for subsequent weighing and GC analysis. Gases exiting the collection flask were analyzed by on-line GC using both TCD and FID detectors. Samples of liquid products were collected during sampling intervals of 2 hours over an approximately 16 hour period of operation. Gas analyses were obtained by GCduring each sampling interval.

Two samples were collected while temperature of the catalyst bed was controlled to three progressively higher temperatures. Each sample was about 7 grams. Operating conditions and results are summarized in Tables I - III.

Net conversion of the methoxy moiety (Net MeO, percent) is an indication of the conversion of groups regardless of origin, i.e., both methanol (MeOH) which has one MeO per mole and dimethyl ether (DME) which has two MeO per mol. Net MeO may be expressed as follows:

$$\text{Net MeO} = 100 \text{ X } \frac{(\text{MeOH} + 2\text{DME})_{\text{feed}} - (\text{MeOH} + 2\text{DME})_{\text{effluent}}}{(\text{MeOH} + 2\text{DME})_{\text{feed}}}$$

EXAMPLE 4

In this example an acidic catalyst was used to convert a liquid feedstream of formaldehyde in methanol under conditions which allowed gas-liquid contacting of the solid catalyst (trickle bed operation). Effluent of the condensation comprised water, methanol, formaldehyde, dimethyl ether, methylal and higher polyoxymethylene dimethyl ethers.

The acidic catalyst was a proton exchanged sulfonic acid based ion exchange resin. This polymeric material is a Bronstead (protic) acid. A tubular quartz reactor was charged with 5 cc of acidic catalyst particles. The tubular quartz reactor (approx. 10 mm inside diameter) was equipped with a quartz thermowell terminating at about the midpoint of the catalyst bed.

A liquid feed solution was prepared in a pressurized 50 mL autoclave using 7.42 grams of paraformaldehyde (95%) and 15.93 grams of methanol. Contents of the autoclave were stirred and heated to temperatures of 130° to 140° C for 1 hour, and then cooled. The resulting solution was fed by a syringe pump into a preheat zone above the catalyst bed. Using mass flow controllers, a gas feed mixture of dimethyl ether and nitrogen was also fed to the top of the reactor.

Liquid products from the reactor were collected in a cool (0°C) 25 mL flask for subsequent weighing and GCanalysis. Gases exiting the collection flask were analyzed by on-line GC using both TCDand FID detectors. Operating conditions and results are summarized in Table IV.

EXAMPLE 5

In this example an acidic catalyst was used to convert a mixture of formaldehyde in methanol under conditions which allowed liquid contacting of the solid catalyst. A liquid feed solution was prepared in a pressurized 50 mL autoclave using 7.4 grams of paraformaldehyde (95%) and 15.9 grams of methanol. Contents of the autoclave were stirred and heated to temperatures of 130° to 140° C for 1 hour, and then cooled. The autoclave was opened and charged with 1.0 gram of catalyst. Contents of the autoclave were heated to reaction temperature for 2 to 3 hours with stirring. After cooling to ambient temperature and settling, the supernatant liquid was sampled for GC analysis and formaldehyde titration analysis. Results are summarized in Table V.

EXAMPLE 6

Products of several condensation runs were composited, and the composite vacuum filtered through a medium glass frit. A 90 gram aliquot of filtrate was shaken with 20 grams of basic ion-exchange resin beads (DOWEX 66) which were then allowed to settle for one hour. The resulting supernatant liquid was then gravity filtered through a medium paper filter. A suitable amount (54 grams) of molecular sieve type 3A, which had been activated by calcination at about 538°C, was mixed into the filtrate, and the mixture allowed to stand overnight at ambient temperatures. Liquid was separated from the sieve by vacuum filtration through a medium glass frit. A 45.97 gram aliquot of this acid-free, dry filtrate was charged to a small distillation apparatus consisting of a 100 mL 3-neck flask, a fractionating column and condenser. The charge was distilled into eight overhead fractions which were collected at temperature cuts according to the following schedule.

Schedule of Overhead and Bottom Temperatures

Fraction Number	Temperatures, °C Overhead	Bottom
1	42 to 46	70 to 94
2	47 to 76	95 to 109
3	77 to 94	110 to 118
4	95 to 100	119 to 127
5	101 to 107	128 to 136
6	108 to 112	137 to 146
7	113 to 123	147 to 162
8	124 to 150	163 to 174

White solids (possibly paraformaldehyde) were observed in the column and condenser during cuts 2 through 4, but not thereafter. Composition of the distilled fraction and bottoms are given in Table VI.

EXAMPLES 7 and 8

In these Examples a catalyst of copper, zinc and selenium was used at several elevated temperatures to convert a liquid feedstream of aqueous methanol and a gaseous feedstream of dimethyl ether, nitrogen and dihydrogen. Effluent of the fixed bed reactor was a gaseous dehydrogenation mixture including formaldehyde, dimethyl ether, dihydrogen and carbon monoxide.

A tubular quartz reactor was charged with 9.27 grams (5 cc) of the CuZnSe particles which had been sieved to 18-40 mesh. The tubular quartz reactor (approx. 10 mm inside diameter) was equipped with a quartz thermowell terminating at about the midpoint of the catalyst bed.

A liquid feed solution was prepared using 13.06 grams of water and 17.33 grams of methanol. The resulting solution was fed by a syringe pump into a preheat zone above the catalyst bed. Using mass flow controllers, a gaseous feedstream of 26.9 percent by volume dimethyl ether, 6.62 volume percent nitrogen and a balance of dihydrogen was also fed to the top of the reactor.

Liquid products from the reactor were collected in a cool (0°C) 25 mL flask for subsequent weighing and GC analysis. Gases exiting the collection flask were analyzed by on-line GC using both TCD and FID detectors. Samples of liquid products were collected during sampling intervals of 40 and 80 minutes over an approximately 6 hour period of operation. Gas analyses were obtained by GCduring each sampling interval.

Samples were collected while temperature of the catalyst bed was controlled to temperatures of about 600°C. Each sample was about 2.5 or 7 grams. Operating conditions and results are summarized in Tables VII and VIII.

EXAMPLE 9

In this Example a silver catalyst in the form of needles was used at several elevated temperatures to provide a source of formaldehyde by oxidative dehydrogenation of dimethyl ether, steam and methanol. A tubular quartz reactor was charged with 3.83 grams (1 cc) of the silver needles. The tubular quartz reactor (approx. 10 mm inside diameter) was equipped with a quartz thermowell terminating at about the midpoint of the catalyst bed. Quartz wool was placed above the catalyst zone to assist in vaporizing liquid feed. The liquid feed solution containing 18.6 percent methanol and 81.4 percent by weight water was fed by a syringe pump into the preheat zone above the catalyst bed. Using mass flow controllers, a gaseous feedstream of 59.93 percent by volume dimethyl ether, 31.59 volume percent nitrogen and 8.48 percent by volume dioxygen was also fed to the top of the reactor. Samples were collected while temperature of the catalyst bed was controlled to temperatures in a range from about 400° to about 650°C. Operating conditions and results are summarized in Table IX.

EXAMPLE 10

In this Example a silver catalyst in the form of needles was used at several elevated temperatures to provide a source of formaldehyde by nonoxidative dehydrogenation of dimethyl ether and steam. The liquid feed of water was fed by a syringe pump into the preheat zone above the catalyst bed. Using mass flow controllers, a gaseous feedstream of 89.1 percent by volume dimethyl ether and 10.9 volume percent nitrogen was also fed to the top of the reactor. Samples were collected while temperature of the catalyst bed was controlled to temperatures in a range from about 400° to about 650°C. Operating conditions and results are summarized in Table X.

For the purposes of the present invention, "predominantly" is defined as more than about fifty percent. “Substantially" is defined as occurring with sufficient frequency or being present in such proportions as to measurably affect macroscopic properties of an associated compound or system. Where the frequency or proportion for such impact is not clear, substantially is to be regarded as about twenty per cent or more. The term "essentially" is defined as absolutely except that small variations which have no more than a negligible effect on macroscopic qualities and final outcome are permitted, typically up to about one percent.

Table I
Conversion of Feedstreams at about 100° C Using a Crystalline Borosilicate Catalyst Exhibiting the MFI Crystal Structure

Temperature, ° C		100	101
Run Time, min		95	155
Gas Feed, mol percent			
	Nitrogen	32.925	32.925
	DME	67.075	67.075
Liquid Feed, weight percent			
	Methanol	55.20	55.20
	Formaldehyde	38.55	38.55
	Water	6.25	6.25
Feed Rates			
	Gas scc/min	34.1	34.1
	Liquid mL/min	0.00756	0.00756
Conversions, mole percent			
	Methanol	67.15	66.96
	DME	4.36	2.71
	Net MeO	28.20	27.10
	Formaldehyde	78.84	78.84
Selectivities, percent			
Gases	CO	0	0
	CO_2	0	0
Liquids	Methylal	80.548	78.269
	HPE	0.750	0.751
DME/MeOH		5.38	5.44
Carbon Balance		92.57	93.39

Where MeOH is methanol, HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n value of 2 or more, MeO is methoxy moiety, and DME is dimethyl ether.

Table II
Conversion of Feedstreams at about 130° C Using a Crystalline Borosilicate Catalyst Exhibiting the MFI Crystal Structure

Temperature, ° C		132	131
Run Time, min		245	305
Gas Feed, mol percent			
	Nitrogen	32.925	32.925
	DME	67.075	67.075
Liquid Feed, weight percent			
	Methanol	55.20	55.20
	Formaldehyde	38.55	38.55
	Water	6.25	6.25
Feed Rates			
	Gas scc/min	34.1	34.1
	Liquid mL/min	0.00756	0.00756
Conversions, mole percent			
	Methanol	53.59	53.68
	DME	5.12	4.75
	Net MeO	23.52	23.33
	Formaldehyde	86.71	86.71
Selectivities, percent			
Gases	CO	0	0
	CO_2	0.095	0.086
Liquids	Methylal	64.480	64.699
	HPE	0.323	0.326
DME/MeOH		3.48	3.50
Carbon Balance		91.63	91.53

Where MeOH is methanol, HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1, MeO is methoxy moiety, and DME is dimethyl ether.

Table III
Conversion of Feedstreams at about 160° C Using a Crystalline Borosilicate Catalyst Exhibiting the MFI Crystal Structure

Temperature, ° C		164	160
Run Time, min		345	400
Gas Feed, mol percent			
	Nitrogen	32.925	32.925
	DME	67.075	67.075
Liquid Feed, weight percent			
	Methanol	55.20	55.20
	Formaldehyde	38.55	38.55
	Water	6.25	6.25
Feed Rates			
	Gas scc/min	34.1	34.1
	Liquid mL/min	0.00756	0.00756
Conversions, mole percent			
	Methanol	34.82	35.19
	DME	7.45	1.12
	Net MeO	17.84	14.05
	Formaldehyde	90.59	90.59
Selectivities, percent			
Gases	CO	0	0
	CO_2	0.370	0.317
Liquids	Methylal	42.970	43.410
	HPE	0.094	0.096
DME/MeOH		2.37	2.54
Carbon Balance		92.40	94.76

Where MeOH is methanol, HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1, MeO is methoxy moiety, and DME is dimethyl ether.

Table IV

Trickle Bed Conversion of Feedstreams Using an Ion Exchange Resin Based Catalyst Exhibiting Bronstead Acid Sites

Temperature, ° C	71
Feed Rates	
Gas scc/min	10
Liquid mL/min	0.0756
Conversions, mole percent	
Methanol	87.04
Formaldehyde	92.27
Selectivities, percent	
Methylal	97.78
HPE	1.77

Where HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1.

Table V

Liquid Phase Conversion Using an Ion Exchange Resin Based Catalyst Exhibiting Bronstead Acid Sites

Temperature, ° C	67
Conversions, mole percent	
Methanol	73.38
Formaldehyde	77.91
Selectivities, percent	
Methylal	88.20
HPE	6.03

Where HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1.

COMPOSITION OF OVERHEAD FRACTIONS AND BOTTOMS

	Compound				$CH_3O(CH_2O)_nCH_3$ where the value of n is:					
Fraction	Methylal	Methanol	Hemiacetals	Trioxane	2	3	4	5	6	7
Starting	49.95	0.0	0.69	2.42	22.60	12.42	6.40	3.15	1.45	0.61
1	97.21	0.95	0.05	0.0	0.46	0	0	0	0	0
2	93.83	2.52	0.38	0.0	2.84	0	0	0	0	0
3	20.81	12.92	8.85	2.39	54.80	0.17	0	0	0	0
4	3.24	11.12	6.40	4.49	74.19	0.57	0	0	0	0
5	0.56	8.47	2.29	5.83	82.07	0.78	0	0	0	0
6	0.40	3.10	0.16	7.21	88.05	1.08	0	0	0	0
7	0.43	0.99	0.0	9.38	86.60	2.55	0.05	0	0	0
8	0.32	0.47	0.0	11.77	82.98	4.37	0.08	0	0	0
Bottoms	0.29	0.02	0.0	0.54	1.10	49.49	26.19	13.05	6.34	2.96

Table VII

Dehydrogenation of Dimethyl Ether at about 600° C
Using a Catalyst of Copper, Zinc and Selenium

Temperature, ° C	599	596
Run Time, min	40	80
Gas Feed, mol percent		
Nitrogen	6.62	6.62
DME	26.90	26.90
Dihydrogen	66.48	66.48
Liquid Feed, weight percent		
Methanol	57.03	57.03
Water	42.97	42.97
Feed Rates		
Gas scc/min	135	135
Liquid mL/min	0.07563	0.07563
Conversions, mole percent		
Methanol	55.62	58.29
DME	17.33	14.87
Net MeO	27.75	26.69
Selectivities, percent		
CO	3.66	3.27
CO_2	13.94	15.08
Formaldehyde	66.29	67.15
Methylal	0	0
HPE	0..311	0..312
DME/MeOH	6.07	6.75
Carbon Balance	92.57	93.39

Where HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1, MeO is methoxy moiety, and DME is dimethyl ether.

Table VIII
Dehydrogenation of Dimethyl Ether at about 600° C Using a Catalyst of Copper, Zinc and Selenium

Temperature, ° C	599	596
Run Time, min	210	275
Gas Feed, mol percent		
Nitrogen	6.62	6.62
DME	26.90	26.90
Dihydrogen	66.48	66.48
Liquid Feed, weight percent		
Methanol	57.03	57.03
Water	42.97	42.97
Feed Rates		
Gas scc/min	135	135
Liquid mL/min	0.07563	0.07563
Conversions, mole percent		
Methanol	51.17	51.70
DME	13.64	16.33
Net MeO	23.63	25.95
Selectivities, percent		
CO	2.78	2.80
CO_2	15.15	17.31
Formaldehyde	70.63	68.01
Methylal	0	0
HPE	0..318	0..306
DME/MeOH	5.96	5.83

Where HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1, MeO is methoxy moiety, and DME is dimethyl ether.

Table IX
Oxidative Dehydrogenation of Dimethyl Ether Using a Catalyst of Silver Needles

Temperature, ° C	397	508
Run Time, min	60	100
Gas Feed, mol percent		
Nitrogen	31.59	31.69
DME	59.93	59.93
Dioxygen	8.48	8.48
Liquid Feed, weight percent		
Methanol	18.6	18.6
Water	81.4	81.4
Feed Rates		
Gas scc/min	146	146
Liquid mL/min	0.4125	0.4125
Conversions, mole percent		
Methanol	9.21	10.55
DME	15.44	16.41
Net MeO	14.01	15.08
Dioxygen	94.40	93.85
Selectivities, percent		
Light Alkanes	1.37	4.07
CO	18.19	20.15
CO_2	9.06	7.92
Formaldehyde	56.57	59.16
Methylal	0	0
HPE	0	0
DME/Methanol	3.23	3.20

Where HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1, MeO is methoxy moiety, and DME is dimethyl ether.

Table IX Continued
Oxidative Dehydrogenation of Dimethyl Ether Using a Catalyst of Silver Needles

Temperature, ° C	614	660
Run Time, min	150	195
Gas Feed, mol percent		
Nitrogen	31.59	31.69
DME	59.93	59.93
Dioxygen	8.48	8.48
Liquid Feed, weight percent		
Methanol	18.6	18.6
Water	81.4	81.4
Feed Rates		
Gas scc/min	146	146
Liquid mL/min	0.4125	0.4125
Conversions, mole percent		
Methanol	13.53	15.30
DME	17.18	23.94
Net MeO	16.34	21.96
Dioxygen	94.28	94.53
Selectivities, percent		
Light Alkanes	19.47	28.59
CO	25.41	20.15
CO_2	5.29	3.39
Formaldehyde	45.79	37.70
Methylal	0	0
HPE	0	0
DME/Methanol	3.30	3.10

Where HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1, MeO is methoxy moiety, and DME is dimethyl ether.

Table X
Nonoxidative Dehydrogenation of Dimethyl Ether Using a Catalyst of Silver Needles

Temperature, ° C	408	511
Run Time, min	115	175
Gas Feed, mol percent		
Nitrogen	10.9	10.9
DME	89.1	89.1
Liquid Feed, weight percent		
Water	100	100
Feed Rates		
Gas scc/min	102	102
Liquid mL/min	0.07563	0.07563
Conversions, mole percent		
DME	3.63	2.56
Net MeO	3.63	2.56
Selectivities, percent		
Light Alkanes	46.21	46.48
CO	0	0
CO_2	0	0
Formaldehyde	53.79	53.52
Methylal	0	0
HPE	0	0

Where HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1, MeO is methoxy moiety, and DME is dimethyl ether.

Table X Continued
Nonoxidative Dehydrogenation of Dimethyl Ether
Using a Catalyst of Silver Needles

Temperature, ° C	612	650
Run Time, min	290	465
Gas Feed, mol percent		
Nitrogen	10.9	10.9
DME	89.1	89.1
Liquid Feed, weight percent		
Water	100	100
Feed Rates		
Gas scc/min	102	102
Liquid mL/min	0.07563	0.07563
Conversions, mole percent		
DME	9.38	23.39
Net MeO	9.36	23.28
Selectivities, percent		
Light Alkanes	53.06	52.51
CO	5.51	14.96
CO_2	0.34	0.25
Formaldehyde	41.10	32.29
Methylal	0	0
HPE	0	0

Where HPE is higher polyoxymethylene dimethyl ethers which are $CH_3O(CH_2O)_nCH_3$ having n greater than 1, MeO is methoxy moiety and DME is dimethyl ether.

That which is claimed is:

1. A process for catalytic production of a mixture of oxygenated organic compounds suitable as a blending component of fuel for use in compression ignition internal combustion engines, which process comprises providing a source of formaldehyde formed by conversion of methanol in the presence of a catalyst comprising silver as an essential catalyst component; and contacting the source of formaldehyde and a predominately dimethyl ether feedstream with a condensation promoting catalyst capable of hydrating dimethyl ether, in a form which is heterogeneous to the feedstream, under conditions of reaction sufficient to form an effluent of condensation mixture comprising water, methanol, formaldehyde, dimethyl ether, one or more polyoxymethylene dimethyl ethers having a structure represented by the type formula

$$CH_3O(CH_2O)_nCH_3$$

in which formula n is a number from 1 to about 10.

2. The process according to claim 1 wherein the conditions of reaction including temperatures in a range from about 50° to 130°C, and the condensation promoting catalyst capable of hydrating dimethyl ether comprises at least one member of the group consisting of molecular sieves.

3. The process according to claim 2 wherein the molecular sieve is crystalline borosilicate exhibiting the MFI crystal structure, and has the following compositions in terms of mole ratios of oxides:

$$0.9\pm0.2\ M_{2/n}O : B_2O_3 : Y\,SiO_2 : Z\,H_2O,$$

wherein M is at least one cation having a valence of n, Y is between 4 and about 600, and Z is between 0 and about 160.

4. The process according to claim 2 which further comprises fractionating the effluent of condensation to obtain an

overhead stream, which is predominantly dimethyl ether, and an essentially dimethyl ether-free bottom stream comprising formaldehyde, methanol and at least methylal, and heating the bottom stream with an acidic catalyst, which is heterogeneous to the feedstream, under conditions of reaction sufficient to convert formaldehyde and methanol present to methylal and higher polyoxymethylene dimethyl ethers.

5. The process according to claim 4 wherein the heating of the bottom stream with the acidic catalyst employs at least one catalytic distillation column with internal and/or external stages of contact with the acidic catalyst, and internal zones to separate the methylal from the higher polyoxymethylene dimethyl ethers.

6. The process according to claim 5 wherein the mixture of polyoxymethylene dimethyl ethers is contacted with an anion exchange resin disposed within a section of the distillation column below the stages of contact with the acidic catalyst to form an essentially acid-free mixture.

7. The process according to claim 6 wherein the essentially acid-free mixture of polyoxymethylene dimethyl ethers is fractionated within a section of the distillation column below the stages of contact with the acidic catalyst to provide an aqueous side-stream which is withdrawn from the distillation column, and an essentially water-free mixture of polyoxymethylene dimethyl ethers having values of n greater than 1 which mixture is withdrawn from the distillation column near its bottom.

8. The process according to claim 7 wherein at least a portion of the aqueous side-stream is used for recovery of an aqueous formaldehyde solution in an adsorption column.

9. The process according to claim 4 wherein the at least a portion of the overhead stream containing dimethyl ether is recycled to the contacting with the condensation-promoting catalyst of claim 1.

10. The process according to claim 2 wherein the source of formaldehyde is formed by a process comprising continuously contacting a gaseous feedstream comprising methanol, dioxygen and diluent gas with a catalytically effective amount of an oxidative dehydrogenation promoting catalyst comprising silver as an essential catalyst component at elevated temperatures to form a gaseous mixture comprising formaldehyde, methanol, dioxygen, diluent gas, carbon dioxide and water vapor; cooling the gaseous mixture to predominantly condense water and adsorb formaldehyde therein; and separating the resulting liquid source of formaldehyde from a mixture of gases comprising methanol, dioxygen, diluent gas, carbon dioxide and water vapor.

11. The process according to claim 10 wherein the contacting of the gaseous feedstream with the oxidative dehydrogenation promoting catalyst is carried out at temperatures in a range from about 590° to about 620°C.

12. The process according to claim 10 wherein the oxidative dehydrogenation promoting catalyst comprises silver and optionally up to about 8 percent by weight of a compound selected from the group consisting of oxides of boron, phosphorous, vanadium, selenium, molybdenum and bismuth, phosphoric acid, ammonium phosphate and ammonium chloride.

13. The process according to claim 10 wherein the source of dioxygen is air.

14. The process according to claim 10 wherein the formaldehyde formed is recovered as an aqueous solution containing from about 5 to about 25 percent methanol less than about 40 percent water by using at least one continuous adsorption column with cooling to temperatures in a range downward from about 100°C to 15°C.

15. The process according to claim 10 wherein the source of dioxygen is a dioxygen enriched gas stream obtained by physically separating a gaseous mixture, containing at least about

10 volume percent dioxygen, into a dioxygen depleted stream and a dioxygen-enriched gas stream.

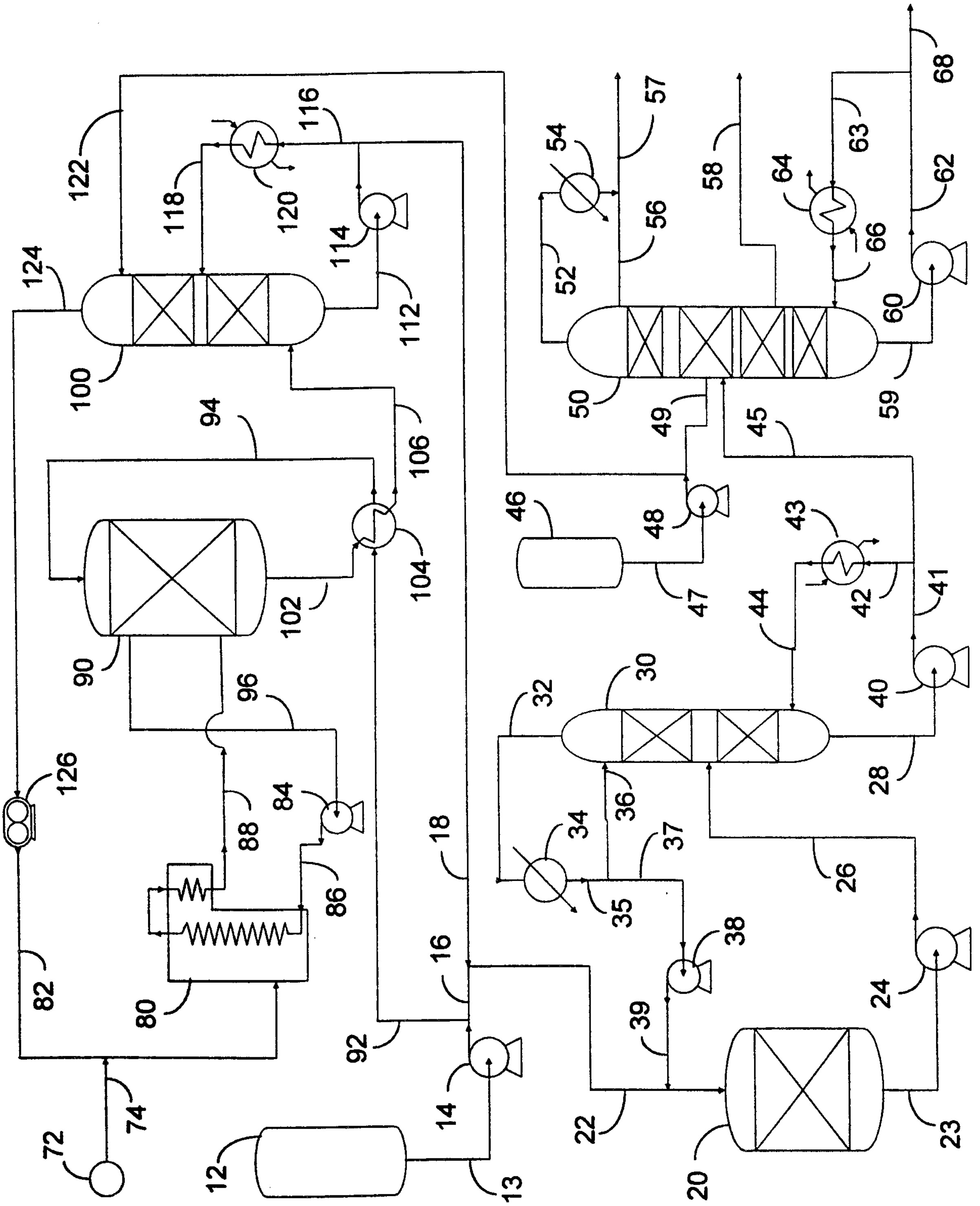
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FIG. 1

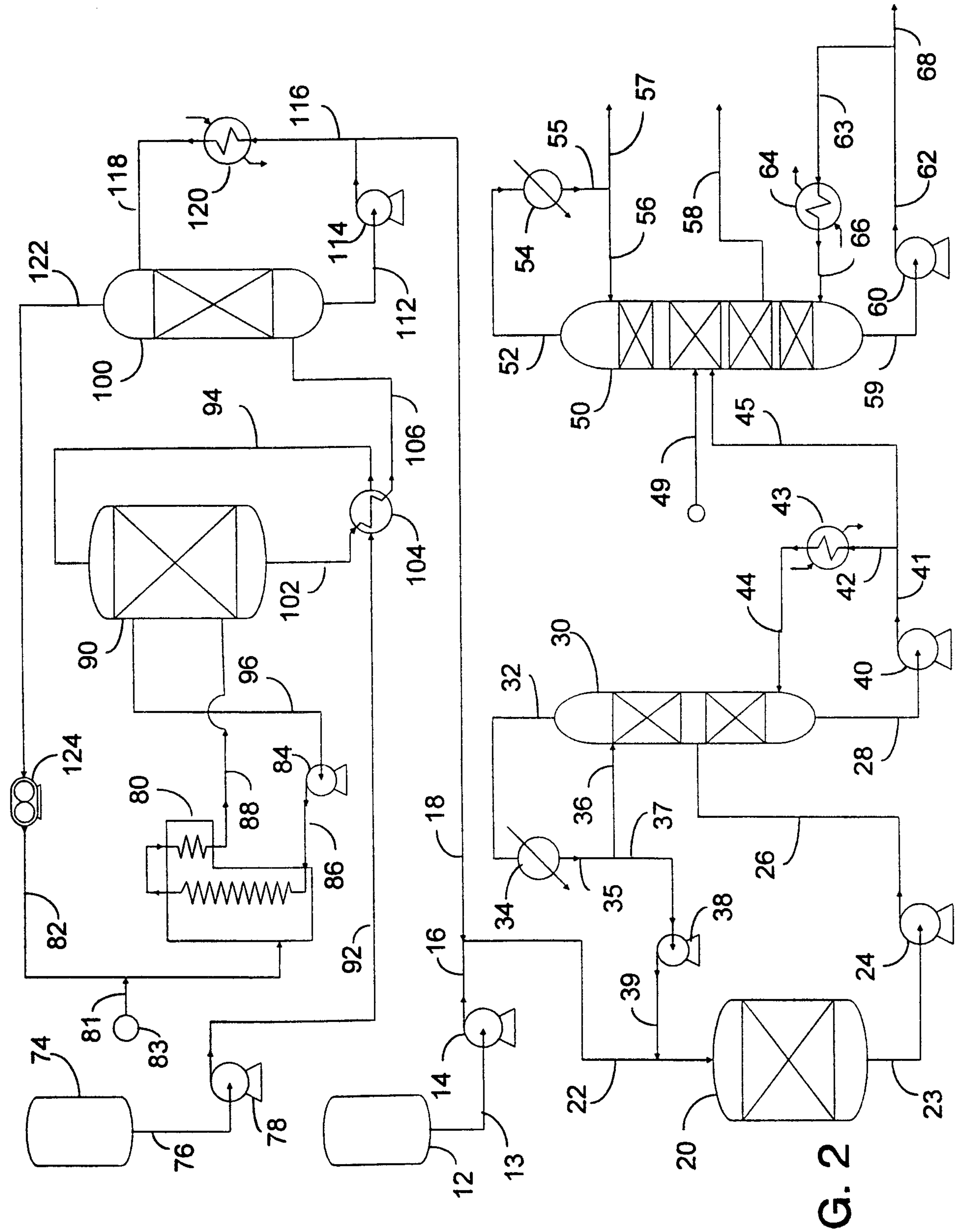
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FIG. 2

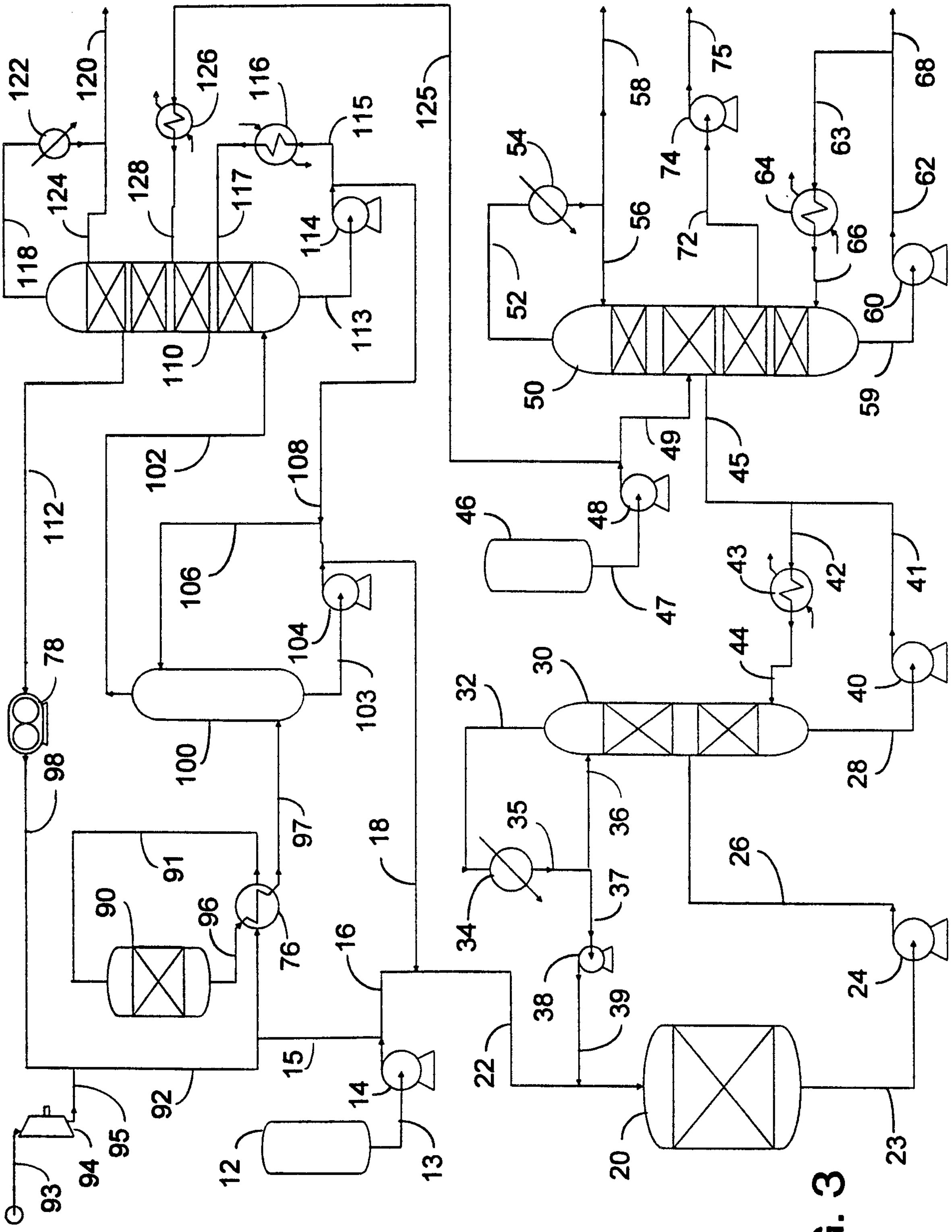
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FIG. 3

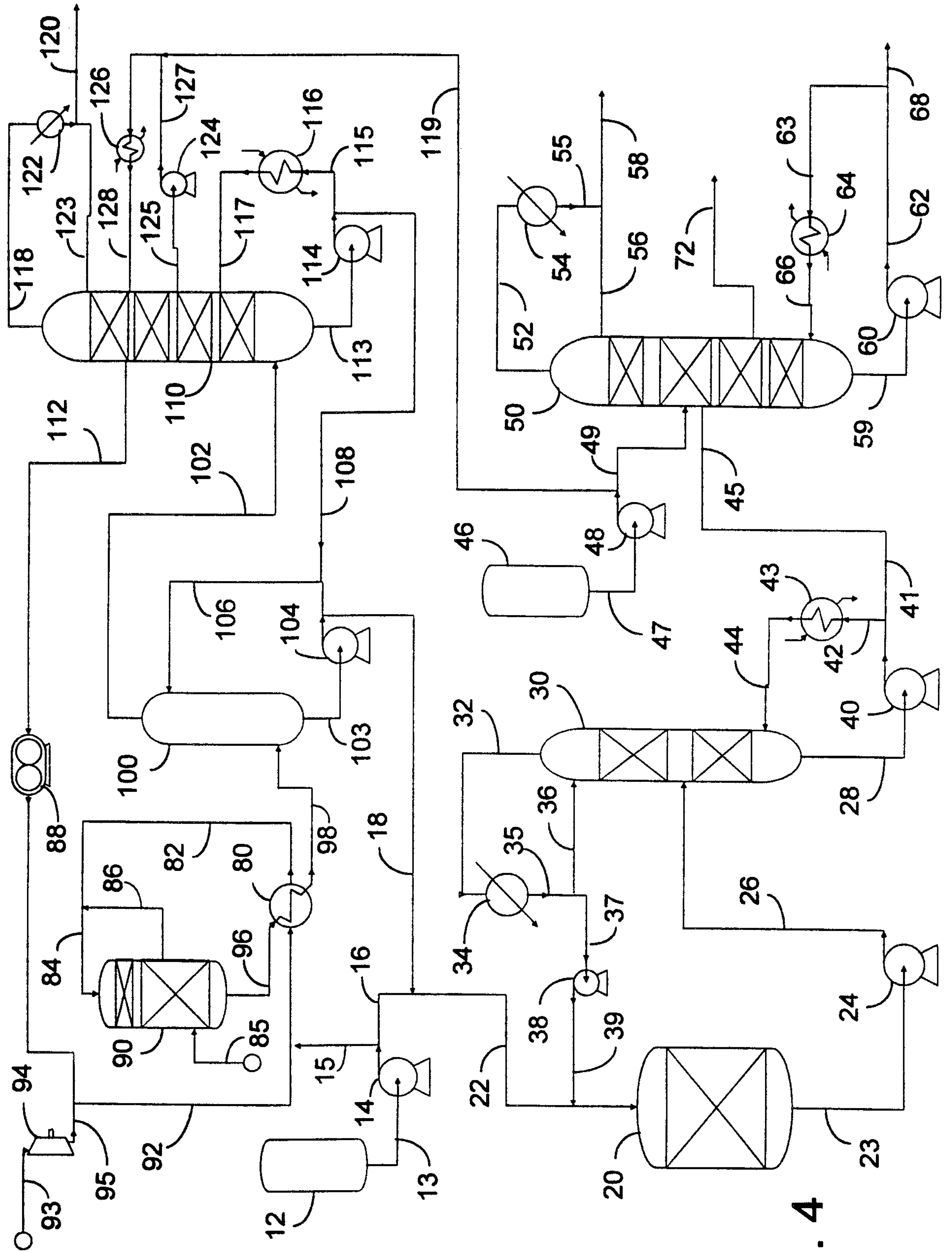
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FIG. 4

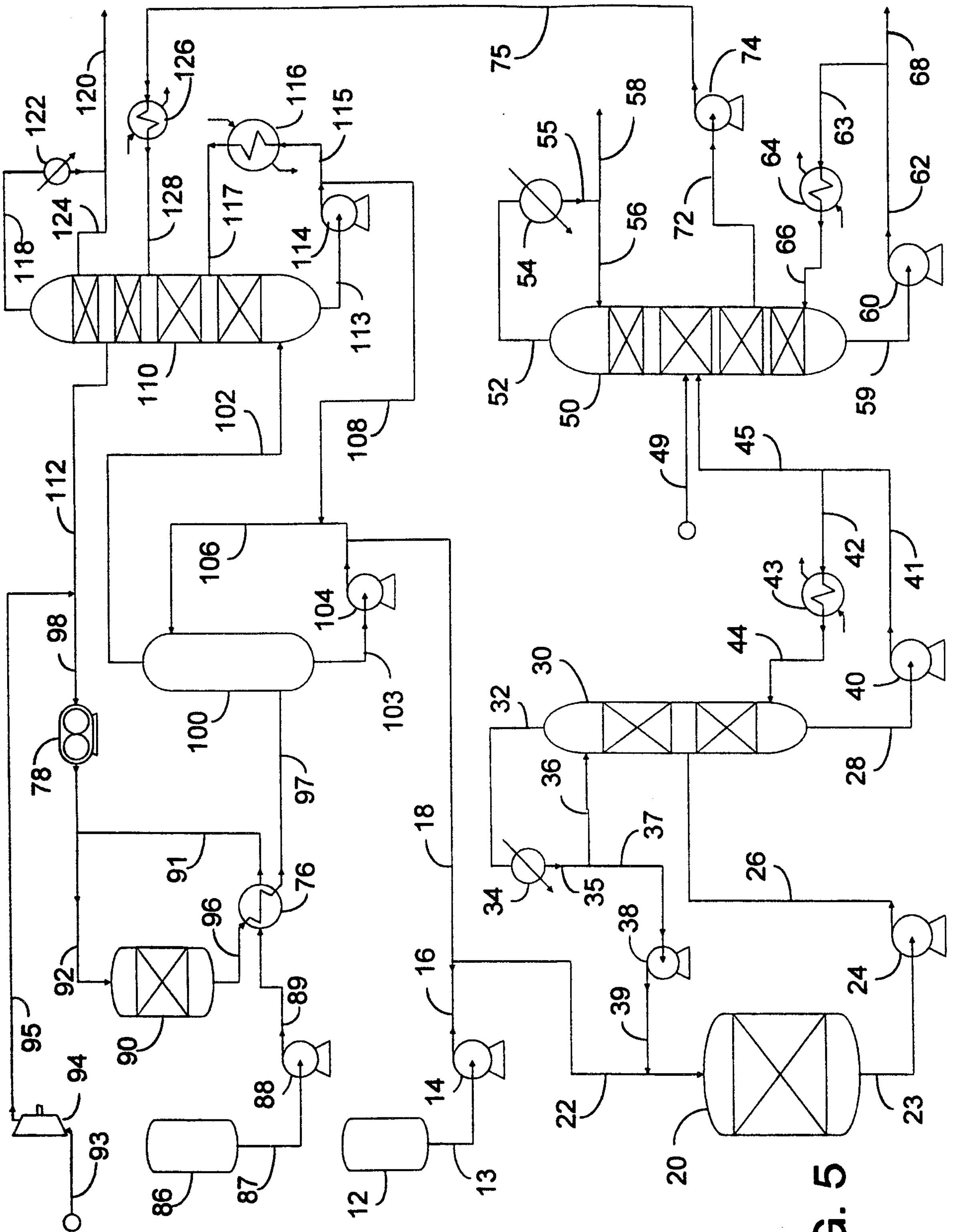
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FIG. 5

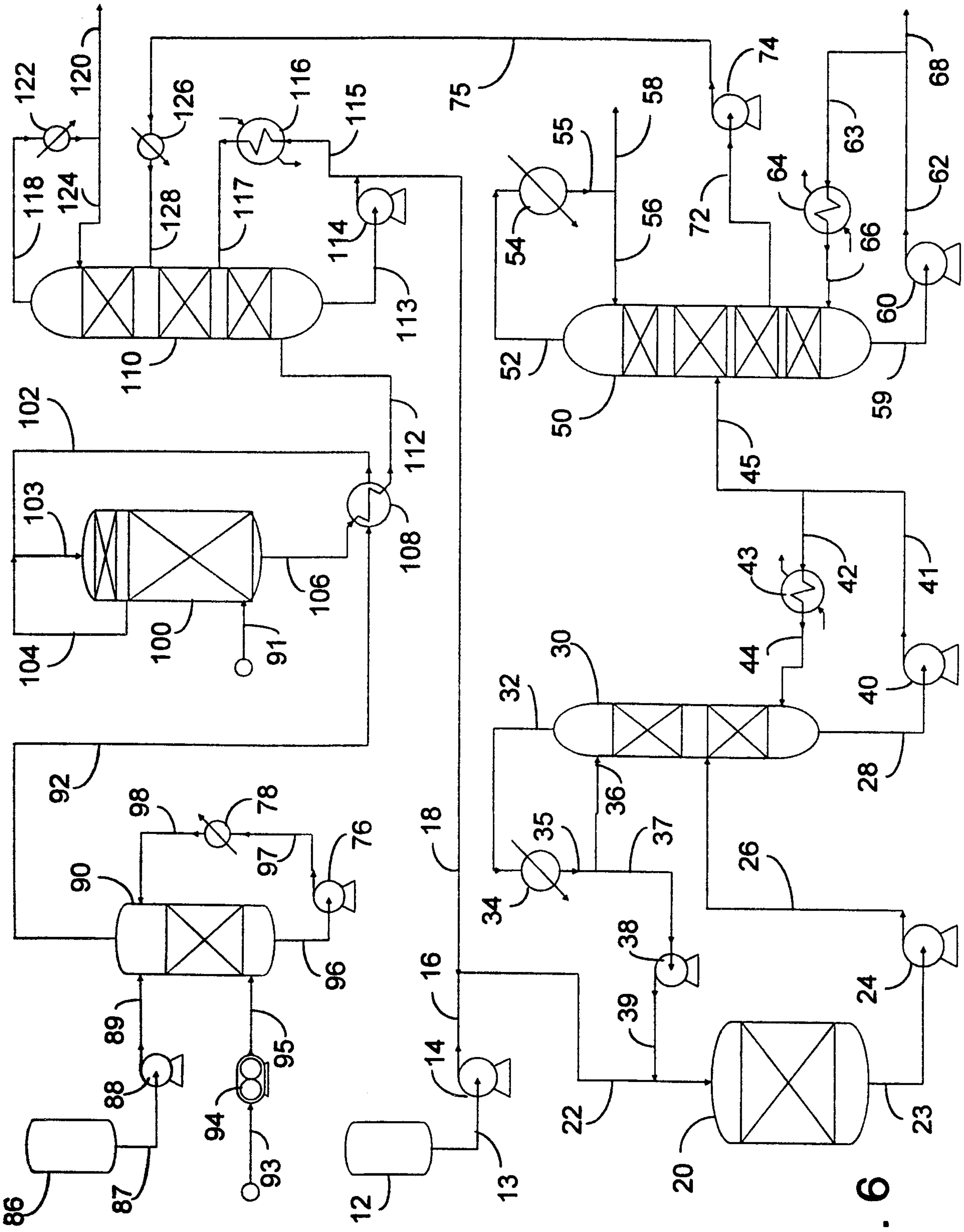
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FIG. 6

INTERNATIONAL SEARCH REPORT

Inter onal Application No
PCT/US 99/20439

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C41/56 C07C43/04 C07C43/30 C07C45/38 C10L1/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 746 785 A (MOULTON DAVID S ET AL) 5 May 1998 (1998-05-05) cited in the application the whole document ---	1
A	DD 245 868 A (LEUNA WERKE VEB) 20 May 1987 (1987-05-20) cited in the application the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 17 December 1999	Date of mailing of the international search report 24/01/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Goetz, G

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INTERNATIONAL SEARCH REPORT

nformation on patent family members

Inter. ›nal Application No
PCT/US 99/20439

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5746785 A	05-05-1998	WO 9902626 A	21-01-1999
DD 245868 A	20-05-1987	NONE	