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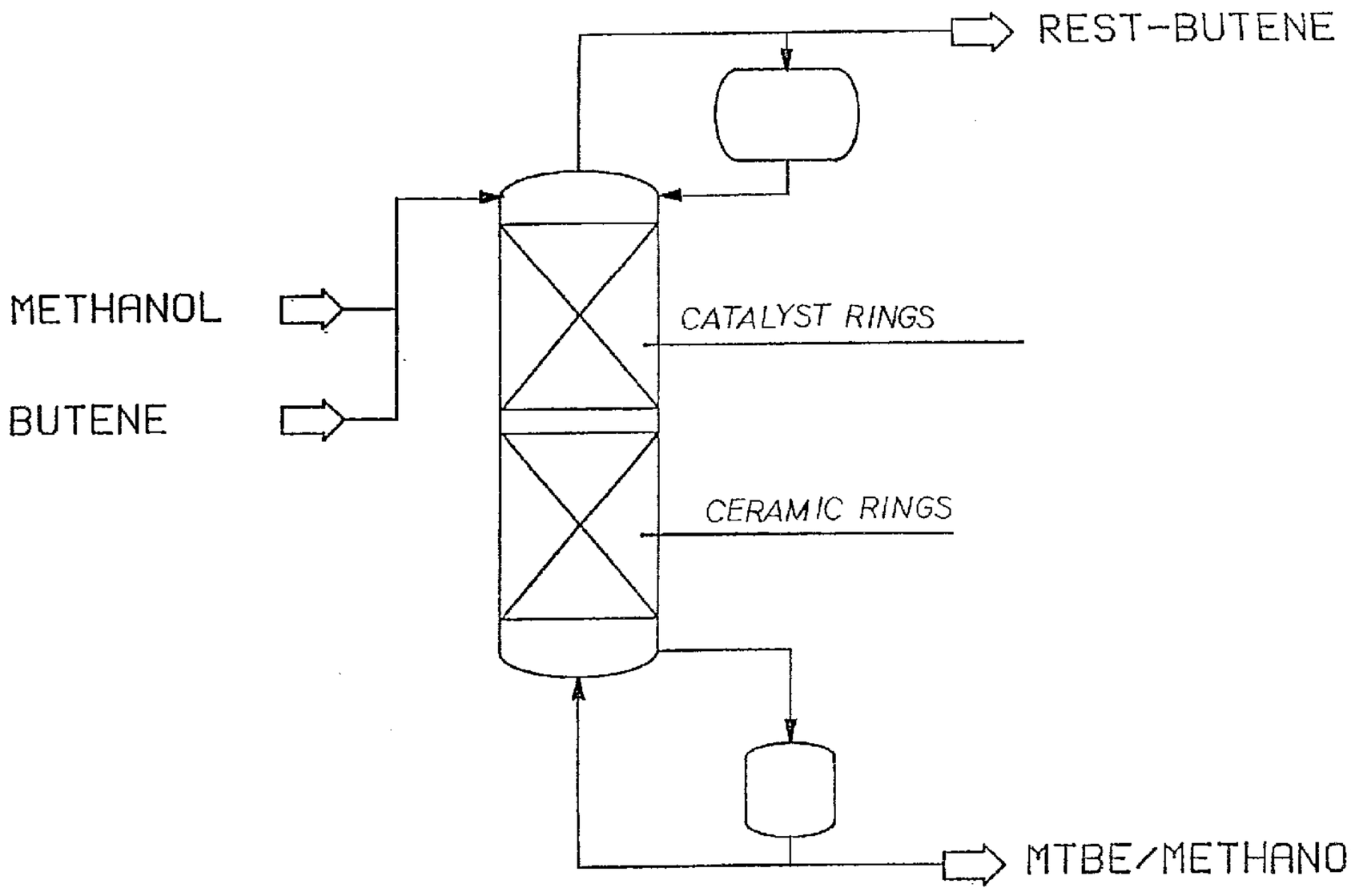
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(54) **CORPS FACONNES DE RESINES ECHANGEUSES D'IONS MACROPOREUSES ET METHODE D'UTILISATION CONNEXE**

(54) **SHAPED BODIES OF MACROPOROUS ION EXCHANGE RESIN AND METHOD OF USING SAME**



(57) Shaped bodies are made of an acid or basic macroporous ion exchange resin. The shaped bodies may be used as packing material in chromatography columns and have substantially the shape of Raschig rings, Berl saddles, Torus saddles, other rings having a web or cross-webs, pall-rings, hollow bodies or hollow spheres. The shaped bodies have a proportion of cavities of 5 to 95% by volume of the macroform, a BET-surface of 0.01 to 1000 m^2/g and an exchange capacity of 0.05 to 10 meq/g. The shaped bodies are provided with catalytic activity through an endowment with a metal or metals of Groups VII and VIII of the periodic table. Such catalytically active shaped bodies may be used for chemical reactions such as etherification, hydration, dimerization, oligomerization, esterification, hydrogenation, hydration or alkylation or combinations thereof. Use of the shaped bodies in combinations of the above reactions with separation operations such as adsorption, absorption, extraction, stripping, distillation, rectification, fractionation or membrane processes and the like is preferred.

ABSTRACT

Shaped bodies are made of an acid or basic macroporous ion exchange resin. The shaped bodies may be used as packing material in chromatography columns and have substantially the shape of Raschig rings, Berl saddles, Torus saddles, other rings having a web or cross-webs, pall-rings, hollow bodies or hollow spheres. The shaped bodies have a proportion of cavities of 5 to 95% by volume of the macroform, a BET-surface of 0.01 to 1000 m^2/g and an exchange capacity of 0.05 to 10 meq/g. The shaped bodies are provided with catalytic activity through an endowment with a metal or metals of Groups VII and VIII of the periodic table. Such catalytically active shaped bodies may be used for chemical reactions such as etherification, hydration, dimerization, oligomerization, esterification, hydrogenation, hydration or alkylation or combinations thereof. Use of the shaped bodies in combinations of the above reactions with separation operations such as adsorption, absorption, extraction, stripping, distillation, rectification, fractionation or membrane processes and the like is preferred.

SHAPED BODIES OF MACROPOROUS ION EXCHANGE RESIN AND METHOD OF USING SAME

The invention relates to shaped (molded) bodies made of macroporous ion exchange resins and to a method of using such shaped bodies as packing material in a chromatographic column.

Macroporous ion exchange resins are commonly used as packing materials in chromatography columns. For example, European Published Application EP 0 104 912 describes the separation of sugars through liquid chromatography over a chromatography column packed with a porous sulphonaceous divinylbenzene-styrene copolymer. The particle size of the packing material described is 1 to 30 micrometers.

The catalytic etherification of isobutene and methanol to methyl-tertiary-butylether (MTBE) on a macroporous highly acid ion exchange resin, has been the subject of renewed detailed reaction-technical examinations, the results of which were published in a dissertation of A. Rehfinger, Technical University of Clausthal, 1988. The catalyst used had a particle size of .3 to 1.2 mm.

Japanese Application No. 58 133 821, discloses a process for exchange of the hydrogen isotope deuterium with hydrogen in an equilibrium reaction between hydrogen and water vapor, wherein a platinum loaded hydrophobic catalyst made of styrene-divinylbenzene copolymer is used as carrier material in the form of small spheres, pellets, woven or knitted planar structures, Raschig rings, and the like. The catalyst is held within a netting of high quality steel or plastic resin, which netting affects the passage of liquid water.

The final report of R.P. Arganbright, Dennis Hearn, Edward M. Jones, Lawrence Smith, DOE/CS/40 454-T3, September 1986, all of the Chemical Research and Licensing Company and Neochem Corporation, describes a new process for the manufacture of MTBE through catalytic distillation, which permits the simultaneous catalysis and distillation in one reaction vessel.

The catalyst used was a sulphonaceous divinylbenzene-styrene copolymer of a particle size between .1 and .5 mm, which catalyst was held in pockets of a fiberglass tissue. The pockets were produced by stitching together along their sides belt-like strips of the fiberglass tissue. After filling, the end openings of the pockets were closed by stitching together and a number of filled belts were rolled, together with intermediate mesh structures made of high quality steel having a mesh size of 12 inches, to cylindrical bodies for use in a solid bed reactor column.

It is a disadvantage of these methods that the material transport through the column and within the packing is substantially reduced by the material enclosing the actual ion exchanger.

It is an aspect of the present invention to achieve, in a single apparatus, the combination of a chemical reaction with simultaneous separation of at least one product from the reaction mixture, wherein a catalytically active filler material positioned in the apparatus accelerates the reaction and provides for the intensive component exchange required with such a reaction combination.

This is achieved through shaped bodies comprising an acid or basic macroporous ion exchange resin for use as packing material, having substantially the shape of Raschig rings, Berl saddles, Torus saddles, other rings having a web or cross-webs, pall rings, hollow bodies or hollow spheres, and having a proportion of cavities of 5 to 95% by volume of the macroform with pores, a BET-surface of 0.01 to 1000, preferably 20 to 60, m^2/g and an exchange capacity of 0.05 to 10, preferably 3 to 6, meq/g.

The BET-surface was measured in accordance with the one point method of Haul-Dümbgen (DIN 66132). In the chemical technology, shaped bodies are preferably used for enlargement of the reaction surface and for acceleration of reactions between gaseous or vaporous materials or liquids in parallel flow or counterflow arrangements. The shaped bodies are preferably manufactured by means of copolymerization of styrene and divinylbenzene in a weight ratio of 200:1 to 1:8, preferably 20:1 to 5:1, by using a

polymerization initiator, for example, through the addition of a free radical initiator. If required, a pore generating agent may be added to the total mixture in an amount of 2 to 80%, preferably 10 to 40% by weight. An important group of shaped bodies may be manufactured from a highly acid macroporous ion exchange resin by generating acidic centers, especially through a subsequent acid treatment, for example, with sulphonic acid. For certain reactions, it is preferred to endow the shaped bodies as described above with metals of Groups VII and VIII of the periodic table, especially palladium, platinum, ruthenium or rhodium, in an amount of 0.1 to 100 g/1 of ion exchange resin. The above described shaped bodies preferably have the same outer shape as Raschig rings with an inner diameter of 0.5 to 100 mm, preferably 4 to 20 mm, a wall thickness of 0.1 to 20 mm, preferably 0.5 to 3 mm, and a length which corresponds to 0.1 to 20 times the inner diameter.

The invention further provides for the use of the above described shaped bodies as catalytically active filler elements for chemical reactions or combinations of chemical reactions, especially etherification, hydration, dimerization, oligomerization, esterification, hydrogenation or alkylation reactions. It is especially preferred to use the shaped bodies in combination with separation operations such as adsorption, absorption, extraction, stripping, distillation, rectification, fractionation, or membrane processes, and the like. The manufacture and use of an ion exchange resin in the form of shaped bodies allows the ion exchanger to be used simultaneously as a filler element for the production of a phase interface and as a catalyst in a filler element reaction column. shaped bodies in accordance with the invention manufactured to have, for example, the same dimensions as a common 7 mm Raschig ring with a wall thickness of 1 mm, permit, for the first time, the achievement of a gap density in a loose filling of ion exchange material, which corresponds to that gap density which is required in a counterflow arrangement with a gaseous or a liquid phase.

In contrast to previous attempts at achieving a corresponding gap density by transforming small individual spheres of a commonly used ion exchange into larger units through interconnection of individual spheres,

the even material thickness achieved in shaped bodies in accordance with the present invention is advantageous for a directed reaction control. Preferred ion exchange resins are divinylbenzene-styrene copolymers, but phenol-formaldehyde resins, uric resins or products of the condensation of aromatic diamines with formaldehyde may also be employed with satisfactory results. The shaped bodies may be manufactured through block polymerization of an appropriate monomer mixture in appropriate moulds, for example, through a ring cleavage polymerization in Teflon (trade mark) moulds. However, other apparatus such as extruders or injection moulding machines, as well as other devices readily apparent to a person skilled in the art and generally used to shape curing polymerization mixtures, may be employed for the forming of the shaped bodies. Gel-like resins may also be used for manufacturing the shaped bodies, which resins are then processed into desired shapes. It is also possible to transfer resins, which are still not fully cured, and thus, still deformable, into appropriate particle moulds and to apply, after shaping of the resin, appropriate hardening conditions for the final hardening of the moulded resin particles in order to reliably achieve the stability required when employing the resulting shaped bodies as packings in industrial apparatus. It is further possible to achieve the desired macroporous structure in accordance with the desired specifications presented above through addition of inert pore generators such as alkanes to the exchange resin, for example, n-pentadecane, in the above mentioned relative proportions. Other auxiliary materials such as polymerization initiator, for example, azoisobutyric acid nitrile (AIBN) or the like, may be added. In highly acid macroporous ion exchange resins made of divinylbenzene cross-linked with polystyrene, SO_3H-groups, which are attached to the polymer matrix through sulphonation, serve as charge carriers and are responsible for the exchange capacity and the catalytic activity of the resin. The aforementioned dimensions of the inner surface, which correspond to the surface of currently sold prior art macroporous types, are achieved through the macroporous structure.

The invention will now be further described by way of the manufacture of a preferred macroporous, highly acid divinylbenzene-styrene copolymer resin.

Example 1

A monomer mixture of styrene and divinylbenzene in a weight ratio of 13 to 1 was prepared. After addition of n-pentadecane as an inert pore generator in an amount of 35% per weight and an effective amount of AIBN as polymerization initiator, the resulting mixture was ready to be poured into a mould. A cylindrical slot defined by Teflon* tubes which are reinforced on the inside and outside, was used as a mould. Two annular segments of Teflon* were used for sealing of the mould and as spacers. The cylindrical slot used had an inner diameter of 4 mm and a width of .5 mm. The mixture was held at 80°C for five hours to achieve completion of the polymerization reaction. Subsequently, the resulting particle blanks were pulled out of the mould and cut to length. The resulting shaped bodies were first washed with chloroform for removal of the n-pentadecane.

For the sulphonation of the shaped bodies, 350 ml of the Raschig rings produced in the above described manner were mixed with 600 ml chloroform and 80 ml chlorosulphonic acid in a flask in an ice cooled bath and kept under return-flow cooling with intermittent mixing for 20 hours for completion of the reaction. Subsequently, an additional 40 ml of chlorosulphonic acid were added and the reaction mixture was left to react for another three to five hours at room temperature. The sulphonated rings were washed first with chloroform then with methanol and finally with water until a pH of 3.0 was reached. The rings were stored in distilled water.

The provision of the highly acid, shaped bodies made of highly acid macroporous resins with one or more metals of Groups VII or VIII of the periodic table, may be achieved by, for example, treating the shaped bodies with a solution of the desired metals, for example, with a solution of corresponding non-complex cationic metal salts in water. Such metal salts may be, for example, the chloride, bromide, nitrate, sulphate and/or acetate. The amount of salt is selected so that, after further treatment,

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especially after reduction, the desired amount of metal is bound to the shaped bodies. After treatment of the shaped bodies with the metal salt solution, the shaped bodies are washed to neutral and dried, for example, at an elevated temperature and at lowered pressure. The transformation of the added metals into their elementary condition is achieved through treatment with a reducing agent, for example, hydrogen, at a pressure of 2 to 50 preferably 20 to 30 bar, and a temperature of 50 to 140°, preferably 80 to 120°C. The shaped bodies are useful as catalytically active filler elements for single phase or multiple phase gas reactions and liquid reactions, especially for counterflow arrangements of the phases, since the particles have a high gap density and thus, cause only a small pressure loss.

The shaped bodies are especially useful as catalytically active filler elements for the carrying out of so-called catalytic distillations, wherein the reaction and the subsequent processing of the reaction products through distillation or rectification, which is normally carried out in a separate processing step, are performed simultaneously in the same reaction vessel.

The installation of the shaped bodies within a reaction vessel is preferably achieved by loose filling of the shaped bodies onto support grates. The entry and exit passages of the reaction vessel may be provided with a sieve web to retain small particles, fragments, abraded particles and the like, or to prevent the dragging along of such particles. The shaped bodies may be placed on a plurality of stacked grates in order to reduce the mechanical load on individual grates.

Especially suited for such a reaction control are chemical reactions wherein the reactants have different boiling points than the reaction products.

The invention will now be further described by way of example and with reference to the following drawings, wherein:

Fig. 1 is a schematic illustration of an application of the shaped bodies in accordance with the invention;

Fig. 2 is a schematic illustration of a variant of the application shown in Fig. 1;

Fig. 3 is a schematic illustration of yet another variant of the application shown in Fig. 1;

Fig. 4 is a schematic illustration of the process used for investigation of the MTBE synthesis kinetics; and

Fig. 5 illustrates an application of shaped bodies in accordance with the invention in a filler element column.

The following exemplary applications which are schematically illustrated in the attached Figures 1 to 3 are of interest:

1. The reaction products have a lower boiling point than the starting mixture. The starting mixture is fed through a conduit 1 into a boiler 5 filled with shaped bodies. The reaction products are separated in a rectification column 6 dependent on their boiling point and are removed through upper and lower drainage conduits 3 and 2 respectively (see Figure 1).

2. The reaction products generated have a higher and lower boiling point than the starting mixture. The starting mixture is supplied through conduit 1 located above a packing of shaped bodies 4 and transformed in the packing into a lower and a higher boiling component. The lower boiling component is removed from the head of the rectification column 6 through upper conduit 3 and the higher boiling component 3 is removed from the sump through lower conduit 2 (see Figure 2).

3. The example illustrated in Figure 3 relates to a case where the stream of starting mixture includes a plurality of components, which have only marginally different boiling points. However, the boiling point of the overall mixture is lower than the boiling point of any of the components.

In this example, the overall mixture includes two starting mixtures 1A and 1B. The stream of starting mixture 1A includes only one component, which has a boiling point slightly above that of reaction product 2, but substantially higher than that of the stream of starting mixture 1B or head product 3. A stream of the higher boiling starting mixture 1A is fed into the top of a rectifier column 5 above a filling of catalyst rings 4, and a stream of the lower boiling mixture 1B is fed into rectifier column 5 below the catalyst filling. In accordance with their boiling points, the components of material stream 1A generally accumulate in the lower half of the column and the components of material stream 1B generally accumulate at the top of the column. However, on the way to the lower half of the column, the components of material stream 1A highly selectively combine with one component of material stream 1B to form a stream of a very high boiling product 2 which may be removed from the sump of the column. The distillate 3 thus reduced by one component may be fed to subsequent processes (Figure 3).

The "catalytic distillation" provides, in addition to the advantage that one processing step is saved and thus, apparatus costs are much reduced, other advantages with respect to the control of the process. This process, which is more advantageous for exothermic reactions, allows the direct use of the freed reaction heat for a simultaneous distillation of the reaction products. The reaction temperature is selected so that it corresponds with the boiling point of the reaction product, which provides for an easy temperature control. The generated reaction product is immediately removed from the reaction zone through the simultaneous distillation, which substantially prevents the generation of subsequent or parallel products. In such a reaction set up, equilibrium reactions may substantially go to completion since the reaction products are removed immediately after their generation and thus, in accordance with the equilibrium constant, new reaction products are continuously generated. Reactions, which may be carried out under the principle of catalytic distillation, are exothermic reactions such as etherification reactions, for example, the manufacture of methyl-tertiary-butylether (MTBE) from methanol and isobutene, hydration reactions, for example, the manufacture of

isopropanol from propene and water, dimerization reactions, for example, of isobutene to di-isobutene, esterification reactions, for example, of acetic acid and isopropanol to isopropyl acetate, alkylation reactions, for example, of phenol and propene to propylphenol and oligomerization reactions, for example, of butene to valuable components of so-called alkylate gasolines.

The shaped bodies in accordance with the invention may also be used as bifunctional catalytically active filler elements in catalyzed reactions such as hydration and etherification reactions with simultaneous hydrogenation. An example of such a reaction is the etherification of light pyrolysis gasoline to tertiary amyl methylether with simultaneous selective hydrogenation of dienes, for example, cyclopentadienes and its derivatives, to the corresponding mono-olefins. The breakdown of MTBE into isobutene and methanol may also be carried out using the processing principle of catalytical distillation. This provides means for recovering highly purified products, in this present case, highly pure isobutene. A further application is the separation of isoamylene from a C5-residue, wherein a tertiary amylalkylether is first produced by way of catalytic distillation, and subsequently, in a second catalytic distillation, broken down into an isoamylene and the alcohol. When used as packing materials in catalytical distillations, the shaped bodies in accordance with the invention have definite advantages over the commercially used small spherical ion exchange material made of a divinylbenzene-styrene copolymer. The shaped bodies in accordance with the invention, when used as filler elements, provide both a phase interface and a catalyst carrier. The successful use of the shaped bodies for the simultaneous processes of catalytical distillation is made possible through the small pressure loss of the shaped bodies. Reaction technological tests have shown that the shaped bodies in accordance with the invention have substantially the same activity as comparable prior art catalysts. Furthermore, it is considered to be especially advantageous to provide an ion exchange resin in the form of shaped bodies, since the particles, because of their high gap density, may be used as filler elements and substantially provide the best possible heat and component exchange between the fluid phases taking part in the reaction. The results of the

comparative tests listed in the following, illustrate, by using the example of the MTBE synthesis, that the shaped bodies made of ion exchange resin are provided with a catalytical activity (example 2) comparable to a commercially available catalyst (in this case Amberlyst* (R) 15), which was used in the tests with an average particle diameter of .2 mm (comparative example 3).

Example 2

For an investigation of the MTBE synthesis reaction kinetics, a reaction mixture, containing the reactants methanol and isobutene and the solvent 1-butene, was fed into a mixing vessel of 106 ml volume through metering pumps. The pumped volume was selected so that the reaction mixture remained in the reaction vessel on average for 5.3 minutes. An illustration of the process in principle is shown in Figure 4.

The catalyst rings were mounted onto a small Teflon* tube in a reaction vessel. Samples were taken from a partial stream of the mixture drained from the reaction vessel, which partial stream was continuously guided through a sampling loop. The results of the test performed on the mentioned parameters are listed below.

No.	Concentrations in % per weight					U_{MeOH} in %
	MeOH	IB	1B	MTBE	DIB	
1	42.7	55.7	-	1.63	-	1.37
2	30.8	57.8	9.43	1.97	-	2.27
3	16.9	60.5	20.0	2.51	0.088	5.12
4	5.96	62.5	29.6	1.40	0.507	7.86
5	4.53	63.1	30.4	1.41	0.556	10.2
6	3.03	63.2	31.5	1.53	0.740	15.5

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reaction speeds
in mmol/s eq

No.	DIB	MTBE
1	-	16.8
2	-	19.5
3	0.66	23.9
4	8.45	29.7
5	9.24	29.8
6	12.2	32.3

Abbreviations: MeOH - methanol
IB - isobutene
MTBE - methyl-tertiary-butylether
DIB - diisobutene
1B - 1-butene

Reaction equations: $MEOH + IB \longrightarrow MTBE$

$IB + IB \longrightarrow DIB$

Reaction conditions: T = 60°C, p = 21 bar

Catalyst filling: 1.0 g Raschig rings made of a highly acid macroporous divinylbenzene-styrene copolymer; dimensions (soaked in water) 6x6x1mm; degree of swelling (dry to wet): 80 volume %; proportion of cavities about 40%; degree of cross-linking: 7.5% by weight of divinylbenzene in monomer mixture with styrene, BET-surface (one-point method N_2 absorption) 30 m^2/g, exchanger capacity 4.5 meq/g.

As will be apparent from the comparison in the following example 3, the initially measured reaction rate was of substantially the same value for the catalyst rings in accordance with the invention and for the Amberlyst* (R)15 catalyst when used under similar conditions.

Example 3 (comparative example)

The following test results were obtained under the same conditions as in example 2 with the one exception that the catalyst elements were of spherical shape and were not fixed within the reaction vessel but kept afloat by a mixer. The total amount of catalyst used was also 1.0g.

No.	Concentrations in % per weight					U_{MeOH} in %
	MeOH	IB	1B	MTBE	DIB	
1	39.2	55.0	5.22	0.544	-	0.502
2	22.0	58.0	19.4	0.549	-	0.898
3	9.2	61.0	28.7	1.02	0.097	3.870
4	4.25	60.3	33.2	1.88	0.295	13.800
5	2.72	60.2	34.3	2.34	0.474	23.800

Reaction rates in mmol/s eq

No.	DIB	MTBE
1	-	18.2
2	-	17.5
3	2.30	31.3
4	6.18	56.8
5	9.21	70.6

Example 4

In additional experiments, the catalyst rings in accordance with the invention were employed in a filler element column made of high grade steel (Wst. Nr. 1,4571). The reactants, methanol and isobutene, were fed into the top end of the column together with the 1-butene solvent. The mixture was heated to a temperature near its boiling point. The upper half of the separator column was filled with chemically active, shaped bodies in accordance with the invention in the form of catalyst rings (Raschig rings), while the lower half of the column was filled with inert ceramic rings of the same dimensions (see Figure 5). The column had an inner diameter of 53 mm. The total height of the shaped elements filling was 1 m. The catalyst rings were supported by three stacked support grates in order to reduce the mechanical loads.

The samples were removed from a partial stream of the top or sump product respectively, which partial streams were continuously guided through sample loops.

In the tables below, the results of repetitions 1 to 9 of the experiment in the above described apparatus using catalyst rings in accordance with the invention, are listed, whereby the stream of the starting components was fed at a speed of 25 ml/min., a pressure in the apparatus of 6 bar (absolute) and a temperature below the catalyst filling of 80°C.

Molar composition of the feed in %

No.	X_{MeOH}	X_{1B}	X_{IB}
1	25.0	63.75	11.25
2	25.0	50.5	24.5
3	25.0	37.5	37.5
4	52.5	23.5	24.0
5	52.5	32.0	15.5
6	52.5	40.5	7.0
7	80.0	10.0	10.0
8	80.0	13.5	6.5
9	80.0	17.0	3.0

Molar composition of the sump product (%)

No.	X_{MTBE}	X_{MeOH}	X_{DI}	$X_{\beta DI}$	X_{Tri}	$X_{\beta Tri}$	IB Umsatz
1	73.08	26.92	traces	0	0	0	58.79
2	84.01	15.99	traces	traces	0	0	70.07
3	67.78	14.48	12.83	4.305	0.28	0.326	79.02
4	44.75	55.25	traces	traces	traces	traces	71.65
5	22.94	76.89	0.085	0.083	traces	traces	69.40
6	9.29	90.71	0	0	0	0	66.06
7	13.52	86.48	0	0	0	0	84.98
8	6.32	93.68	0	0	0	0	80.12
9	3.44	96.56	0	0	0	0	73.69

Abbreviations

MeOH = Methanol
MTBE = Methyl-tertiary-butylether
α-Di = α-Diisobutylene:2,4,4 Trimethyl-1-pentene
ß-Di = ß-Diisobutylene:2,4,4 Trimethyl-2-pentene
α-Tri = α-Triisobutylene:2,4,4,6,6 Pentamethyl-1-heptene
ß-Tri = ß-Triisobutylene:2,4,4,6,6 Pentamethyl-2-heptene
1-B = 1-Butene
IB = Isobutene

It is apparent from the above that the sump product was, in accordance with the invention, substantially free of lower boiling butenes. In addition to the comparative kinetic studies and tests run on the shaped bodies in accordance with the invention used in filler element columns, the results of which are listed above, long term tests on the standing time characteristics of the catalyst in accordance with the invention were performed in a tube reactor with varying catalyst loads.

A V2A-tube of 770 mm length and 20 mm diameter was used, which tube was filled to two thirds with a catalyst in accordance with the invention in the form of Raschig rings. Commercially available C_4-fragments from a refinery, which contain 10 or 49% per weight of isobutene, were used as C_4 mixtures. The results of the etherification of isopropanol or methanol with isobutene under selected conditions are listed in tables 1 and 2.

Unwanted components of the C_4-fragment mixture, which may reduce the activity of the catalyst rings, for example, weak bases such as amines or cations such as sodium, may be effectively removed from the mixture through a washing step with water and a so-called police filter arranged ahead of the entry of the C_4 mixture into the reaction-separation column. Depending on the quality of the methanol input stream, it may be appropriate to use a police filter in the methanol stream as well. Mechanical defects of the catalyst rings were only detected to a minor degree. The catalyst rings of a sulphonated, macroporous styrene polymer were used as hollow cylinders of

about 8 mm height and an outer and inner diameter of about 6 mm. The colour of the hollow cylinders was white to cream. The exchanger capacity was determined by way of the commonly known method (Fisher U. Kunin, Analytical Chemistries 27, 1955, 1191-1194). The swelling volume of 23 mm dry contact in water or methanol, was 50 ml which corresponds to a bulk density when dry of .275 g/ml and when wet of .127 g/ml. The degree of cross-linking of the contact used, corresponds to the nominal proportion of divinylbenzene in the monomeric starting mixture. The BET-surface of the shaped bodies was determined by the one-point method with N_2 adsorption.

The shaped bodies in accordance with the invention in the form of hollow cylinders made of a sulphonated styrene polymer were successfully tested in the following reaction, whereby the same apparatus was used as in the above long term tests, in addition to the tests on the etherification of different i-butene fractions, the results of which were reported above.

1. Hydration of propene with water (Table 3)

2. Hydration of i-butene with water (Table 4)

3. Etherification of 2-Methyl-2-butene with methanol (Table 5)

4. Dimerization of i-C_4 (Table 6).

Furthermore, the hollow cylinders in accordance with the invention made of a sulphonated, macroporous styrene polymer were provided with palladium and tested with respect to their utility as catalysts for the hydrogenating etherification. The loading with palladium was carried out as described below:

.63g $Pd(NO_3)_2 \cdot 2H_2O$ were dissolved in 60 ml of water. The resulting solution was of a brownish-yellow colour. 100 ml of water wet styrene polymer shaped bodies were added to the solution. The styrene polymer was completely covered with the palladium nitrate solution. After standing for

one day, the watery solution was clear, which was a sign for exchange of the palladium.

Commercially available methanol and light gasoline from an olefin plant were used as input materials.

After filling of the shaped bodies into the above described reactor tube, the remaining water in the Raschig rings was forced out with methanol and the palladium was reduced at a temperature of 70°C and a pressure of 11 bar with 6 norm liters of hydrogen in 150 ml methanol per hour. After 48 hours, the methanol was replaced by the gasoline/methanol input mixture of the reaction. The remaining reaction conditions were:

Amount of catalyst: 100 ml (swollen in water);
Temperature: 70 - 75°C;
Pressure: 10 - 11 bar;
Feed material: crack-L-distillate of VC with 10% methanol;
Rate of Feed: 150 ml/h = 103 g/h;
Amount of H_2: 7 NL/h; and
Bi/H_2-Ratio: 200 g/g

The experiment shows that shaped bodies in accordance with the invention, with palladium added, very selectively hydrate the light pyrolysis gasoline which contains polyunsaturated olefins (dienes) and at the same time catalyze the etherification of tertiary mono-olefins with primary and secondary alcohols. For the results of this experiment see Table 7.

TABLE 1

Etherification of C_4-fraction with IPA

Test No.	1	2	3	4	5	6	7	8	9
Catalyst volume swollen (ml)	160	160	160	160	160	160	160	160	160
LHSV (ml input/ml catalyst)	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46	4.92
mol ratio (isobutene: isopropanol)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
input materials									
C_4-fraction (ml/h)	333	333	333	333	333	333	333	333	667
IPA (ml/h)	60	60	60	60	60	120	60	60	120
temperatures, pressure									
entry (°C)	53.2	53.8	54.2	58.6	58.6	58.7	58.6	58.7	58.7
exit (°C)	55.2	56.4	57.2	59.0	59.2	59.2	59.2	59.4	59.5
pressure (bar)	11	11	11	11	11	11	11	11	11
gain of isopropyl-tertiary-butylether	56.0	56.5	56.4	55.6	54.5	51.8	54.4	54.8	46.3
time passed at end of experiment	5	12	30	44	65	79	91	105	119

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TABLE 2

Etherification of i-butene with methanol

Test No.	1	2	3	4	5	6	7
catalyst volume swollen (ml)	200	200	200	200	200	200	200
LHSV (ml input/ml catalyst)	3.98	3.99	4.03	3.97	6.80	6.84	6.85
mol ratio (isobutene: methanol)	0.83	0.83	0.85	0.83	0.84	0.83	0.82
flow rates							
C_4-fraction (g/h)	370.6	371.0	375.6	369.9	633.3	636.3	635.2
methanol (g/h)	124.3	124.8	125.1	123.5	209.4	214.6	216.5
temperatures, pressure							
entry (°C)	59.0	58.0	59.7	60.4	49.1	48.0	49.0
exit (°C)	62.6	62.9	62.6	62.7	67.3	65.2	65.3
pressure (bar)	10	10	10	10	10	10	10
amount of product MTBE (mol-%)	80.1	82.1	83.4	83.3	64.6	60.4	62.1
time passed at end of test (h)	7	14	21	28	35	42	49

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TABLE 3

Hydration of Propene with water

Test No.	1	2	3	4	5	6
catalyst volume swollen (ml)	200	200	200	200	200	200
LHSV (ml input/ml catalyst)	1	1	1	0.5	0.5	0.5
mol ratio (H_2O/C_3)	10.3	9.2	9.8	10.2	10.4	10.3
flow ratios						
propene (g/h)	32.6	32.1	32.2	15.9	15.8	15.7
water (g/h)	142.0	128.0	134.0	69.0	70.0	68.5
exit, stabilized (g/h)	144.2	131.5	139.9	73.2	74.4	73.1
temperatures, pressure						
entry (°C)	120	131	142	139	139	138
exit (°C)	118	128	138	137	137	137
pressure (bar)	80	80	80	80	80	80
IPA-content of the reaction product (% per weight)	2.2	3.8	6.0	8.2	8.5	8.9
conversion of propene(%)	6.8	10.9	18.3	26.4	28.0	29.0
run time of contact at end of experiment	7	14	21	28	35	42

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TABLE 4

Hydration of i-butene with water

Test No.	7	8	9	10	11	12
catalyst volume swollen (ml)	200	200	200	200	200	200
LHSV (ml input/ml catalyst)	0.5	0.49	0.51	0.24	0.22	0.23
mol ratio (H_2O/i-C_4)	10.1	10.2	10.2	12.3	11.2	9.2
flow rates						
i-butene (g/h)	20.2	19.7	20.7	8.4	8.3	9.7
water (g/h)	66.2	65.2	67.6	33.3	29.8	28.6
exit, stabilized (g/h)	67.7	66.9	69.3	34.4	31.0	30.0
temperatures, pressure						
entry (°C)	80.2	80.2	80.1	77.8	78.7	78.9
exit (°C)	79.7	80.2	80.4	79.5	81.3	81.3
pressure (bar)	80	80	80	80	80	80
TBA-content of the reaction product (% per weight)	3.0	3.3	3.0	4.1	5.2	6.1
conversion of i-butene (%)	7.6	8.5	7.6	12.7	14.7	14.3
run time of the contact at the end of experiment (h)	49	56	63	70	77	84

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TABLE 5

Etherification of 2-methyl-2-butene with methanol

Test No.	8	9	10	11	12	13	14	15
catalyst volume swollen (ml)	200	200	200	200	200	200	200	200
LHSV (ml input/ml catalyst)	4.0	4.0	4.0	4.1	2.0	2.0	2.0	2.0
mol ratio (methanol-butene/MeOH)	0.84	0.92	0.91	0.92	0.90	0.89	0.87	0.87
flow rates								
2-methyl-2-butene (g/h)	364.5	374.5	375.3	379.3	185.7	185.2	184.8	184.2
methanol (g/h)	198.6	185.8	187.4	187,9	94.7	95.3	96.6	95.9
temperatures, pressure								
entry (°C)	59.0	58.0	58.0	58.0	61.3	61.2	60.8	61.3
exit (°C)	62.6	61.5	61.9	61.9	59.9	59.8	59.7	59.8
pressure (bar)	10	10	10	10	10	10	10	10
gain of TAME* (mol-%)	26.9	24.3	25.0	23.7	37.3	37.3	37.4	37.5
run time of the contact at the end of experiment (h)	140	147	154	161	168	175	182	189

*TAME = tertiary-amyl-methylether

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TABLE 6

Dimerization of isobutene

Test No.	1	2	3	4	5	6	7
catalyst volume swollen (ml) LHSV (ml input/ml catalyst)	200 1	200 1	200 1	200 1	200 1	200 1	200 2
Input C_4-mixture (g/h) i-butene* (g/h)	118.5 57.8	117.7 57.4	114.3 55.8	113.7 55.9	116.7 56.9	116.7 54.8	233.0 109.5
temperatures, pressure entry temperature (°C) pressure (bar)	73.8 20.0	74.4 20.0	72.2 20.0	72.5 20.0	82.8 20.0	82.6 20.0	90.1 20.0
gain of dimers (mol-%) run time of catalyst (h)	92.9 197	94.4 205	95.8 213	93.5 221	93.5 245	94.3 253	96.3 261

* contained in the C_4-mixture

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TABLE 7

Etherification under hydrogenating conditions

Component		Input	Reaction product
methanol	(% per weight)	10.5	6.8
Σ 2-methylbutene	(% per weight)	17.4	12.8
Σ 2-methylpentene	(% per weight)	5.7	4.6
cyclopentadiene	(% per weight)	0.59	< 0.005
cis-pentadiene-1,3	(% per weight)	0.12	< 0.005
trans-pentadiene-1,3	(% per weight)	0.21	< 0.005
methylbutadiene	(% per weight)	0.11	< 0.005
TAME	(% per weight)	-	6.7
2-methoxi-2-methylpentane	(% per weight)	-	1.5
other oxygen containing components	(% per weight)	-	2.1

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CLAIMS

1. Molded bodies in the form of packing bodies consisting of a macroporous strongly acid or basic ion exchange resin having a voids fraction of 5-95 vol % of the macro shape without pores, a BET surface area of 0.1-1,000 sq m/g, and an ion exchange capacity of 0.05-10 meq/g, which are formed of a macroporous strongly acid or basic ion exchange resin prepared by copolymerizing monomers consisting of styrene and divinylbenzene in a weight ratio of 200:1 to 1:8, in the presence of a polymerization initiator.

2. The molded bodies according to claim 1, which are formed of a macroporous strongly acid ion exchange resin prepared by generating or introducing acid centers therein by subsequent acid treatment.

3. The molded bodies according to claim 1, which are doped with at least one metal of group VIIA or VIIIA of the Periodic Table in amounts of 0.1-100 g/liter of ion exchange resin.

4. The molded bodies according to claim 1, in the form of Raschig rings having an interior diameter of 0.5-100 mm, a wall thickness 0.1-20 mm, and a length 0.1-20 times the interior diameter.

5. The molded bodies according to claim 1, wherein the molded bodies are in the form of Raschig rings, Berl saddles, Torus saddles, packing rings with crossbars, dual intersecting crossbars, pall rings or hollow bodies.

6. The molded bodies according to claim l, wherein said BET surface area ranges from 20-60 sq m/g and said ion exchange capacity ranges from 3-6 meq/g.

7. The molded bodies according to claim 1, wherein said weight ratio of monomers ranges from 20:1 to 5:1 and said copolymerizing is carried out in the presence of a pore former in an amount of from 10-40 wt. % in the entire mixture.

8. The molded bodies according to claim 3, wherein said metal is Pd, Pt, Ru or Rh.

9. The molded bodies according to claim 4, wherein said interior diameter ranges from 4-20 mm and said thickness ranges from 0.5 to 3 mm.

10. The molded bodies according to claim 1, consisting of said macroporous strongly acid or basic ion exchange resin formed of monomer consisting of said styrene and divinylbenzene.

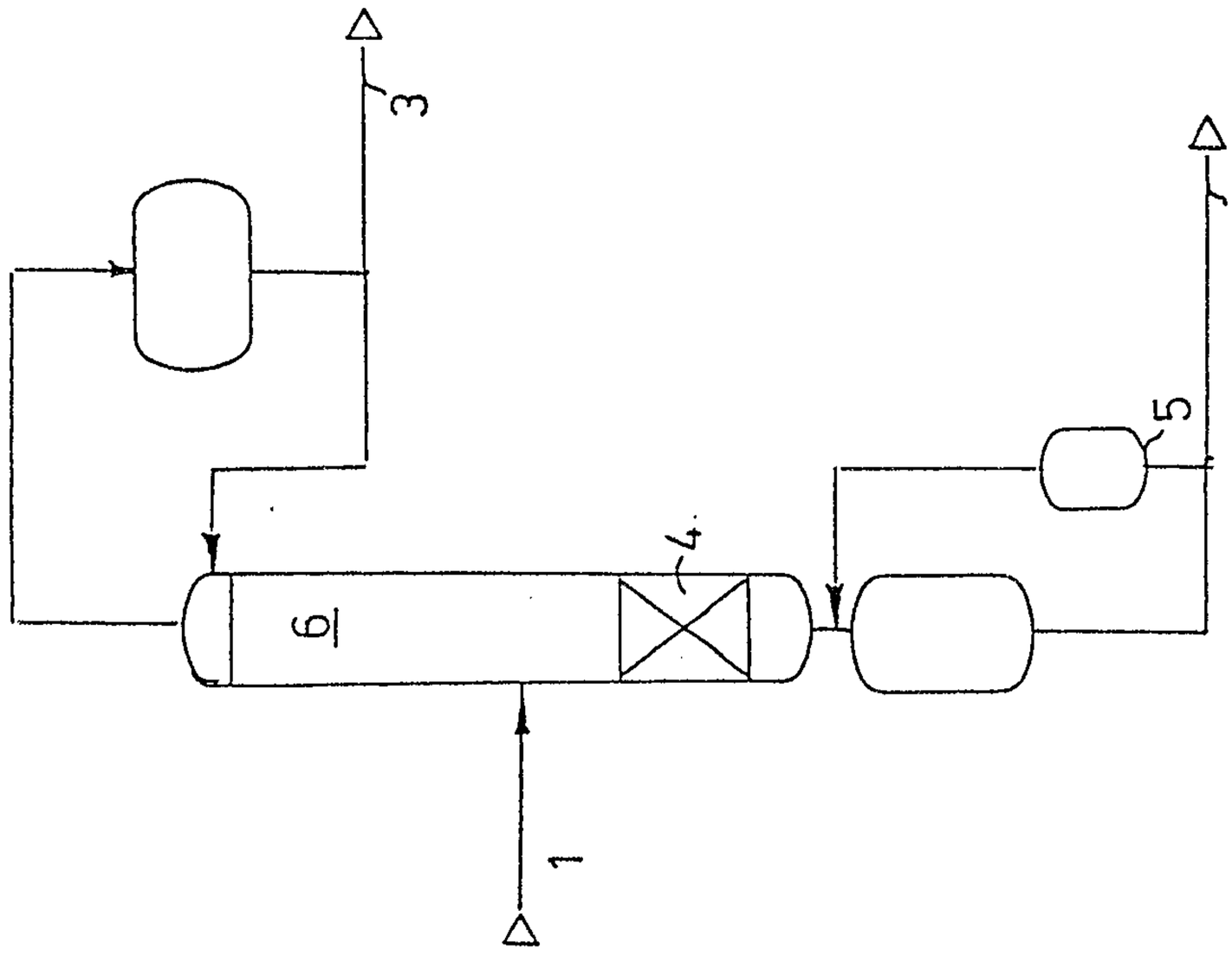


Fig. 2

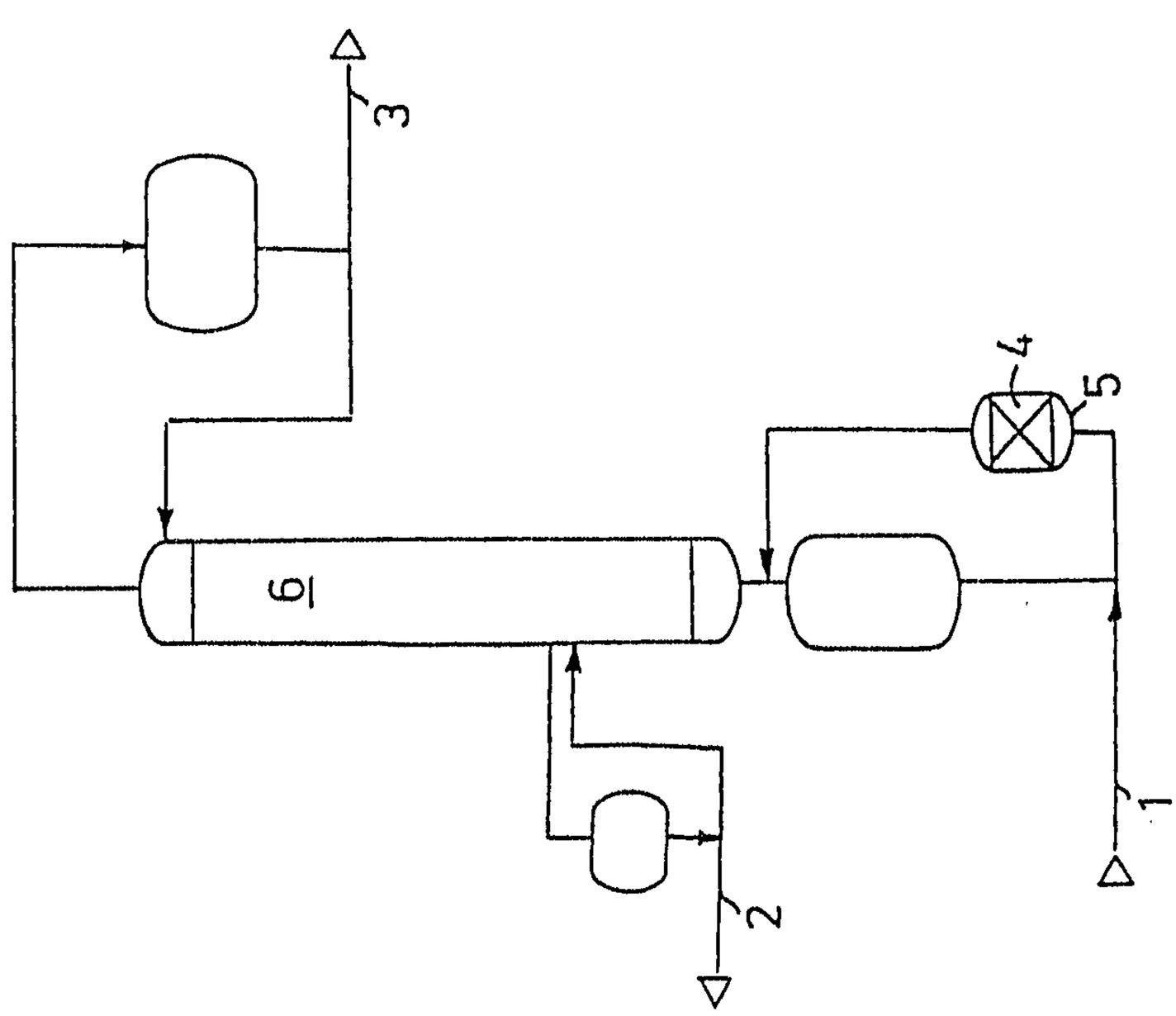


Fig. 1

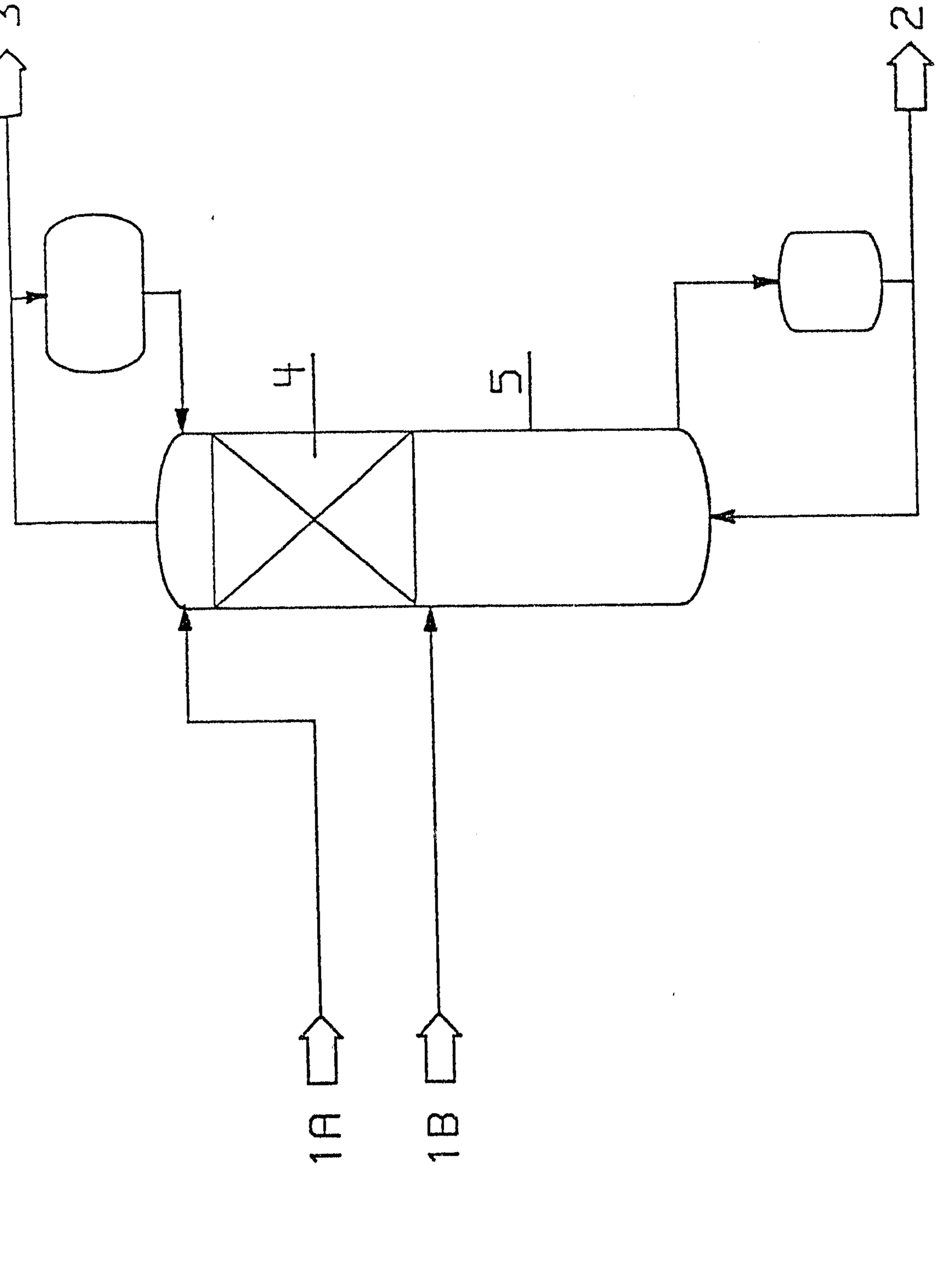


Fig. 3

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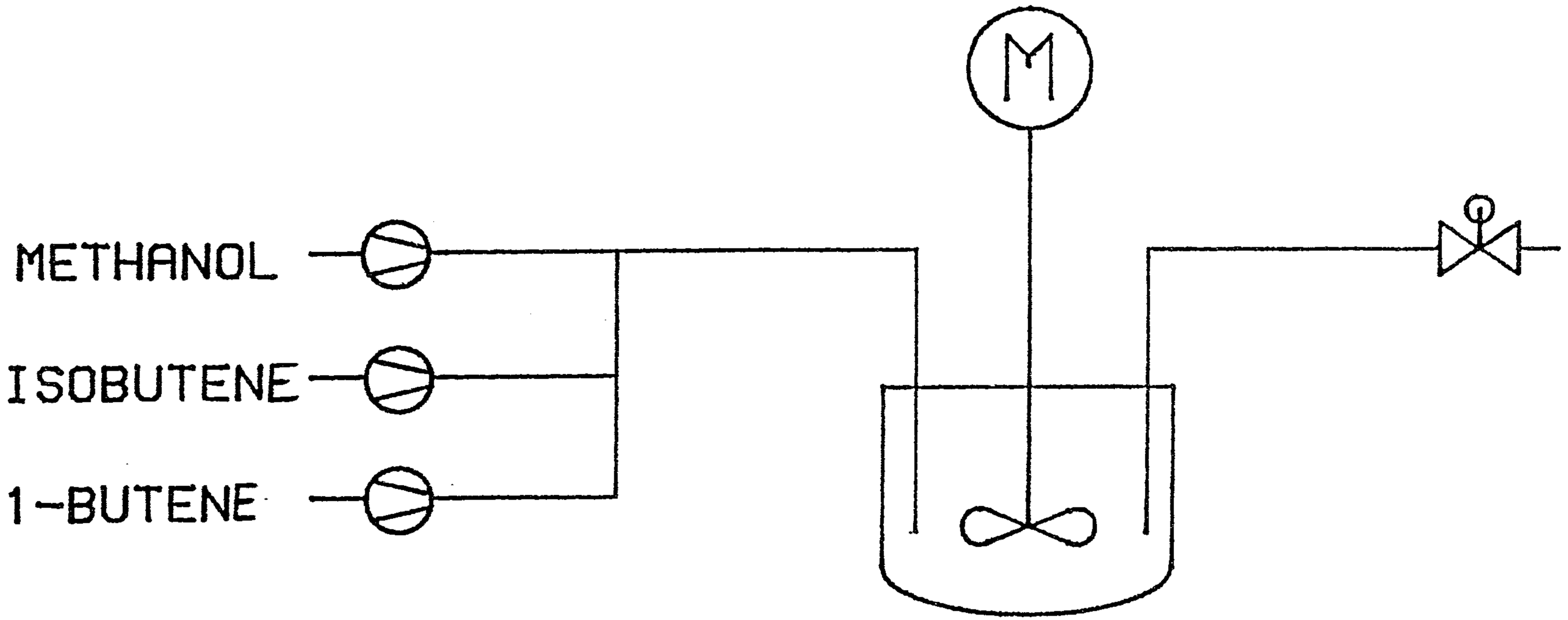


Fig. 4

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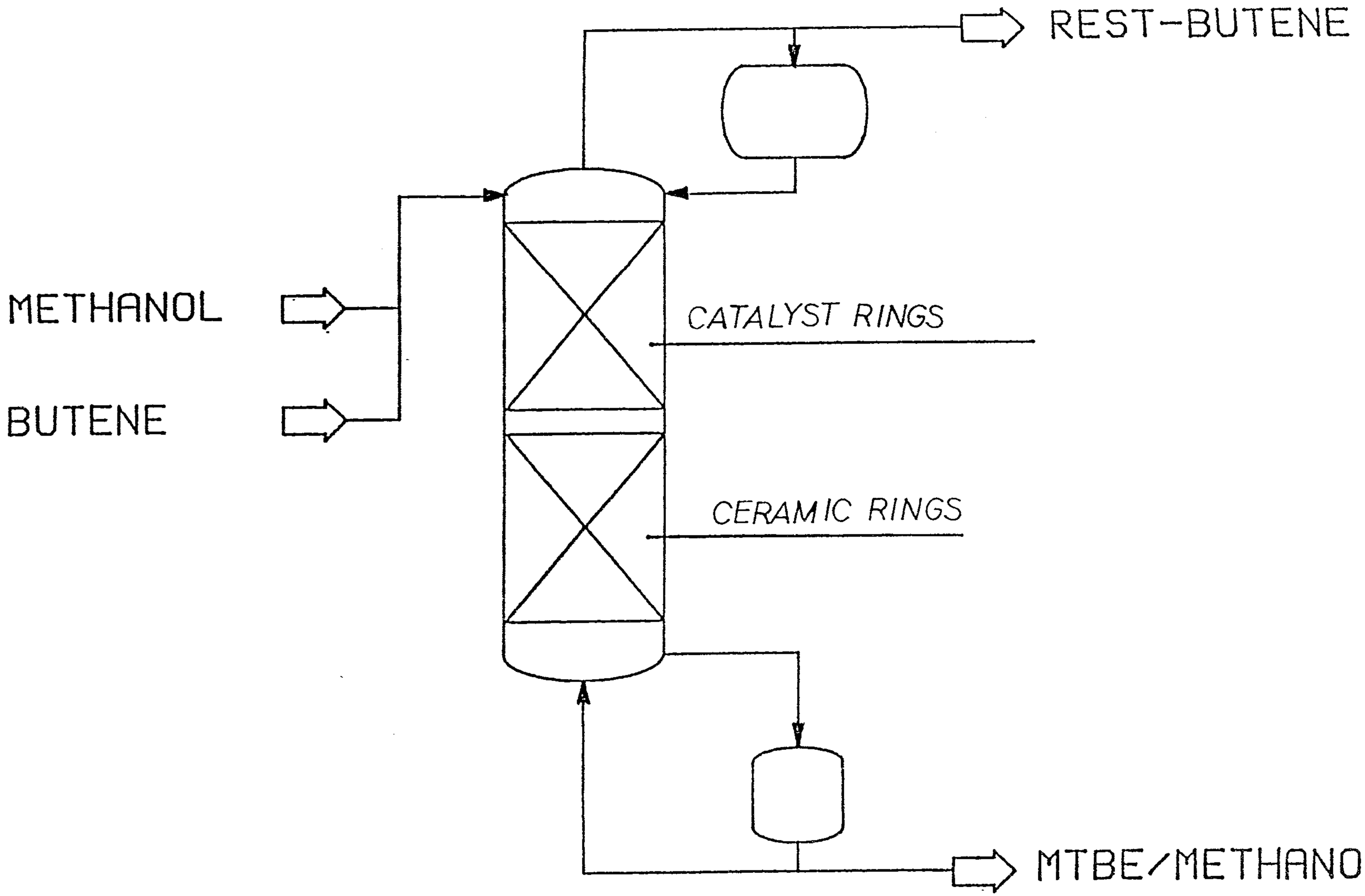


Fig. 5

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