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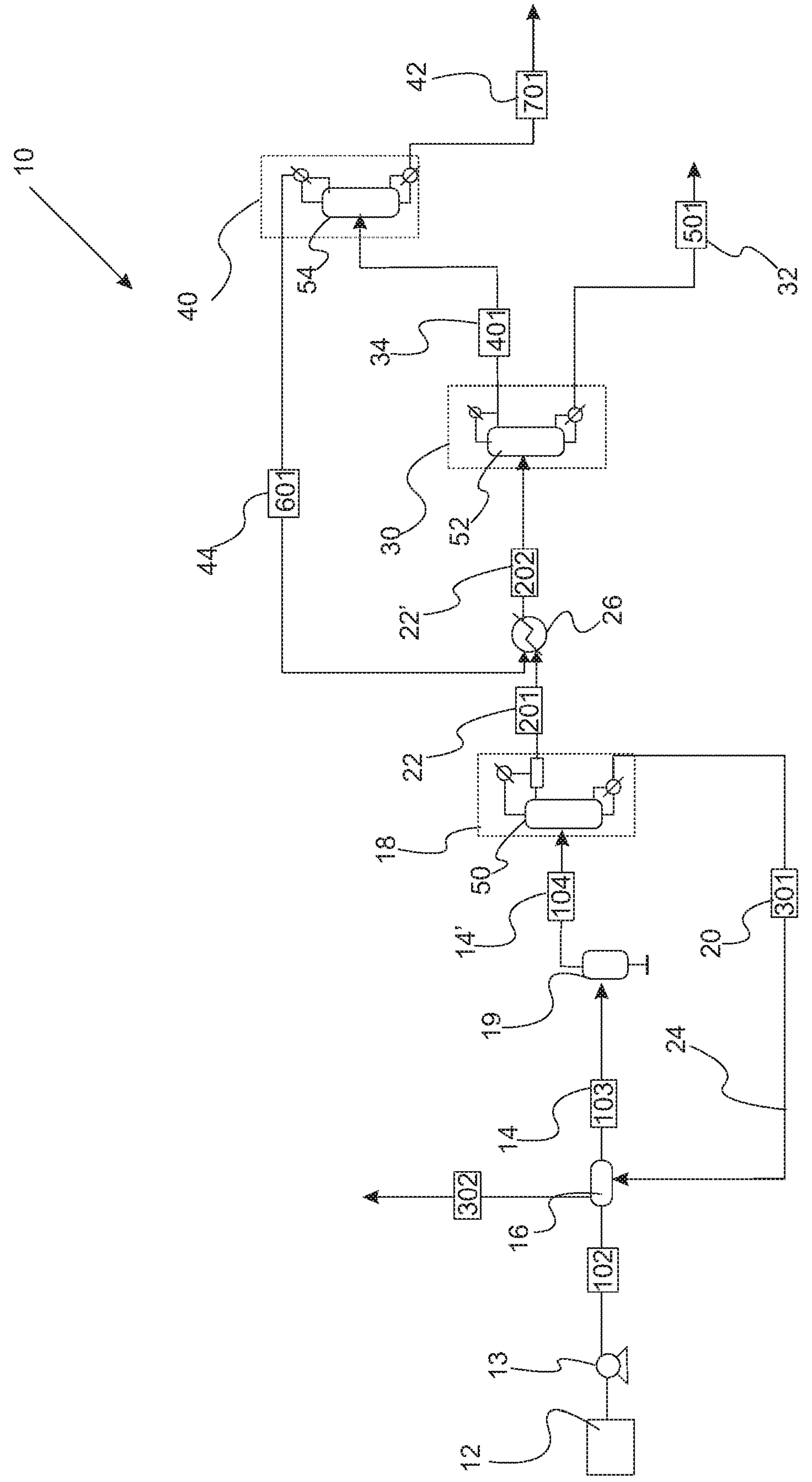
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202
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30
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401
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501
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601
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701

FIG. 1

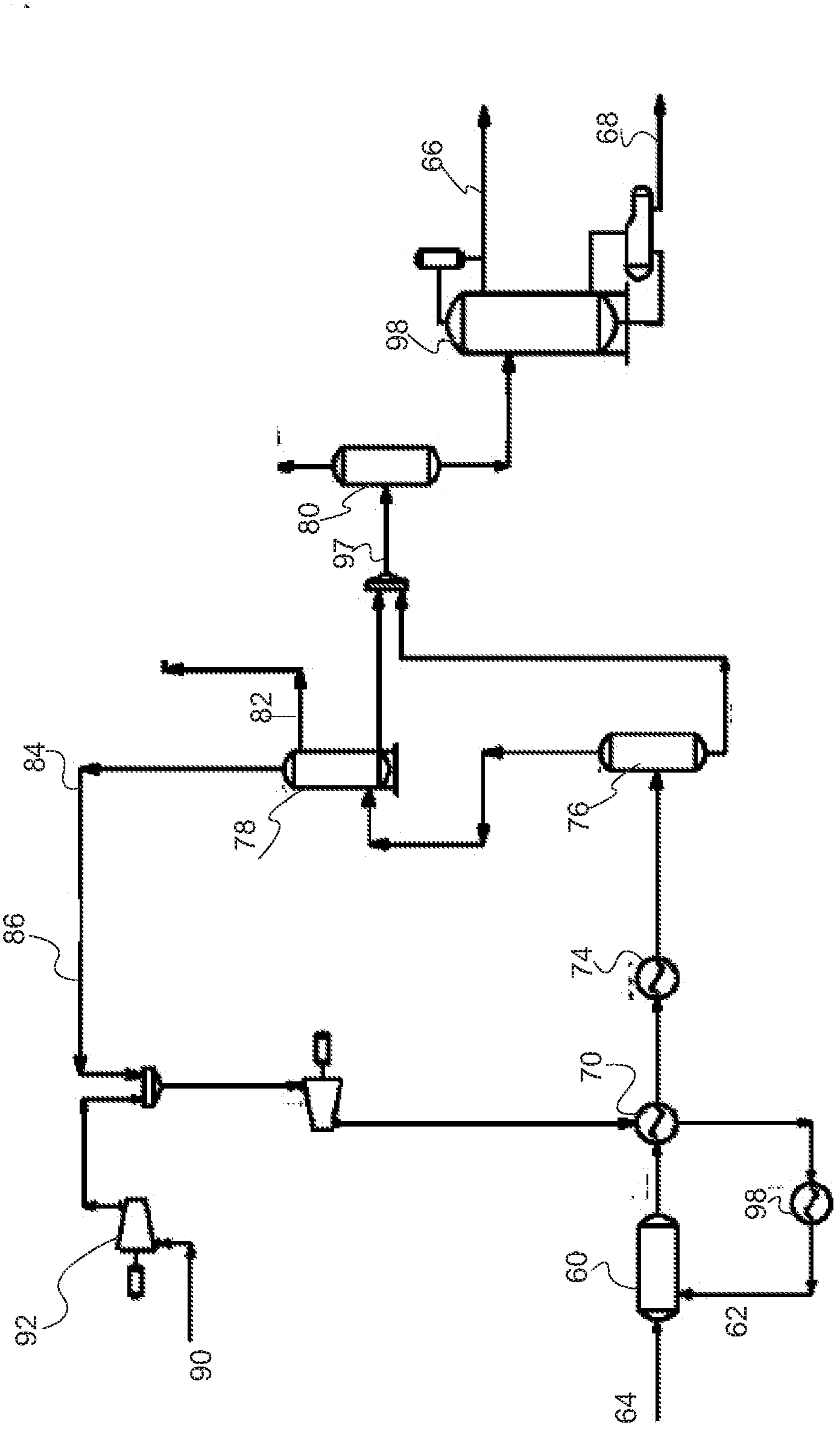

FIG. 2

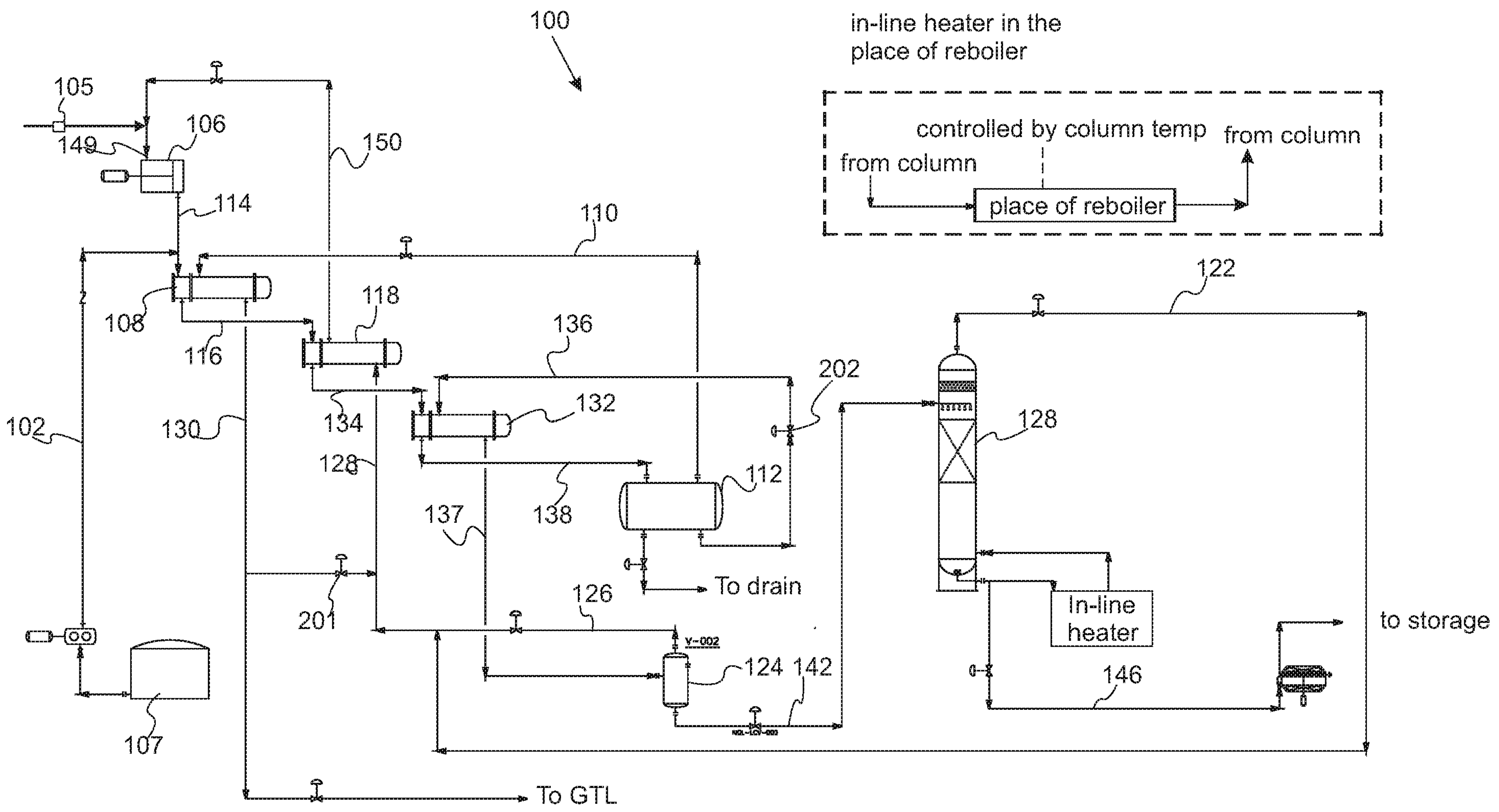
100
in-line heater in the
place of reboiler
controlled by column temp
from column
from column
place of reboiler
105
149
106
114
150
110
108
116
118
136
132
134
102
130
128
202
128
112
137
138
201
To drain
126
V-002
124
142
NGL-LCV-003
122
In-line
heater
146
to storage
107
To GTL

FIG. 3

Table 1.

Mole Fraction	100	101	102	103	104	201	202	301	302	401	501	601	701
ETHANOL	0.0340891	0.0340891	0.0340891	0.0340849	0.0305795	0.0637011	0.0326807	0.0103107	0.0103152	0.0332971	0.0136518	2.90E-10	0.0665943
H2O	0.4065984	0.4066009	0.4069308	0.4250591	0.4069922	0.1017076	0.0522326	0.9587153	0.9580937	1.00E-30	1.63E-13	0	0
FORMALD	5.13E-05	5.13E-05	5.23E-05	1.75E-04	0.1029993	2.60E-05	1.98E-03	4.73E-04	4.12E-05	1.00E-30	8.57E-14	0	0
METHANOL	0.4340015	0.4339993	0.4335896	0.4117019	0.44011	0.5464097	0.2826034	0.01694	0.0175065	0.3996802	1.13E-04	7.48E-04	0.7986125
CH4O2	0.0390817	0.0390792	0.0388358	0.0250754	7.35E-04	1.12E-04	4.12E-06	8.55E-03	9.62E-03	1.00E-30	1.93E-23	0	0
C2H6O3	8.04E-03	8.04E-03	7.96E-03	3.98E-03	1.88E-18	4.49E-07	1.44E-21	2.68E-04	2.41E-04	0	0	0	0
C3H8O4	7.28E-04	7.28E-04	7.20E-04	3.20E-04	8.61E-20	1.13E-09	3.00E-24	8.04E-06	5.67E-06	0	0	0	0
C4H10O5	6.58E-05	6.58E-05	6.50E-05	2.57E-05	4.05E-21	2.86E-12	6.44E-27	2.40E-07	1.33E-07	0	0	0	0
C5H12O6	5.95E-06	5.95E-06	5.87E-06	2.06E-06	1.92E-22	7.19E-15	1.40E-29	7.16E-09	3.12E-09	0	0	0	0
C2H6O2	0.0760462	0.0760485	0.0764416	0.0971938	0.0185835	4.93E-03	6.16E-04	1.78E-03	1.23E-03	1.00E-30	1.29E-09	0	0
C3H8O3	1.25E-03	1.25E-03	1.27E-03	2.29E-03	1.90E-18	4.71E-06	1.32E-20	2.00E-05	8.82E-06	0	0	0	0
C4H10O4	3.46E-05	3.46E-05	3.53E-05	8.99E-05	4.93E-20	7.52E-09	2.19E-23	3.75E-07	1.06E-07	0	0	0	0
C5H12O5	9.49E-07	9.49E-07	9.75E-07	3.51E-06	1.21E-21	1.19E-11	3.45E-26	7.01E-09	1.26E-09	0	0	0	0
C6H14O6	2.60E-08	2.60E-08	2.69E-08	1.37E-07	2.96E-23	1.89E-14	5.23E-29	1.31E-10	1.49E-11	0	0	0	0
ME-ACETA	0	0	0	0	0	0	0	0	0	0	0	0	0
ME-FORMA	0	0	0	0	0	0	0	0	0	0	0	0	0
METHYLAL	0	0	0	0	0	0.2829908	0.6298175	2.92E-03	2.92E-03	0.5670226	3.14E-03	0.999252	0.1347932
POLDME-2	0	0	0	0	0	1.19E-04	6.09E-05	1.76E-05	1.76E-05	1.00E-30	6.47E-03	0	0
POLDME-3	0	0	0	0	0	0	0	0	0	1.00E-30	0.9766289	0	0
POLDME-4	0	0	0	0	0	0	0	0	0	0	0	0	0

Fig. 4

Table 2.

Mass Flow kg/hr	45,36	45,8136	46,2672	47,751	47,174	91,1736	91,6272	13,1236	137	181,894	227.254	272,6136	317,9736
ETHANOL	23,558823	23,5588	23,5588	24,078	23,559	19,6048	19,6048	0,3801	4	19,375	0,229	0,0000	19,37534256
H20	109,884101	109,8847	109,9740	117,420	122.614	12,2405	12,2531	13,8193	144	0,000	0,000	0,0000	0
FORMALD	0.023099	0,0231	0,0235	0,080	51.719	0,0052	0,7780	0,0114	0	0,000	0,000	0,0000	0
METHANOL	208,612908	208,6118	208,4151	202,282	235.828	116,9623	117,9127	0,4343	5	161,759	0,001	0,1514	161,6072926
CH402	28,164709	28,1629	27,9875	18,472	0.591	0,0359	0,0026	0,3285	4	0,000	0,000	0,0000	0
C2H603	9.418351	9,4185	9,3269	4,768	0.000	0,0002	0,0000	0,0168	0	0,000	0,000	0,0000	0
C3H804	1.180749	1,1808	1,1679	0,531	0.000	0,0000	0,0000	0,0007	0	0,000	0,000	0,0000	0
C4H1005	0.136375	0,1364	0,1347	0,054	0.000	0,0000	0,0000	0,0000	0	0,000	0,000	0,0000	0
C5H1206	0.015010	0,0150	0,0148	0,005	0.000	0,0000	0,0000	0,0000	0	0,000	0,000	0,0000	0
C2H602	70,796346	70,7984	71,1645	92,490	19.286	2,0435	0,4978	0,0883	1	0,000	0,000	0,0000	0
C3H803	1,732434	1,7325	1,7537	3,227	0.000	0,0029	0,0000	0,0015	0	0,000	0,000	0,0000	0
C4H1004	0,063421	0,0634	0,0647	0,168	0.000	0,0000	0,0000	0,0000	0	0,000	0,000	0,0000	0
C5H1205	0,002168	0,0022	0,0022	0,008	0.000	0,0000	0,0000	0,0000	0	0,000	0,000	0,0000	0
C6H1406	0,000071	0,0001	0,0001	0,000	0.000	0,0000	0,0000	0,0000	0	0,000	0,000	0,0000	0
ME-ACETA	0,000000	0,0000	0,0000	0,000	0.000	0,0000	0,0000	0,0000	0	0,000	0,000	0,0000	0
ME-FORMA	0,000000	0,0000	0,0000	0,000	0.000	0,0000	0,0000	0,0000	0	0,000	0,000	0,0000	0
METHYLAL	0,000000	0,0000	0,0000	0,000	0.000	143,8586	624,0710	0,1778	2	544,994	0,087	480,2123	64,77820776
POLDME-2	0,000000	0,0000	0,0000	0,000	0.000	0,0842	0,0842	0,0015	0	0,000	0,250	0,0000	0
POLDME-3	0,000000	0,0000	0,0000	0,000	0.000	0,0000	0,0000	0,0000	0	0,000	48,506	0,0000	0
POLDME-4	0,000000	0,0000	0,0000	0,000	0.000	0,0000	0,0000	0,0000	0	0,000	0.000	0,0000	0

FIG. 5

Table 3.

Mass Fraction	100	101	102	103	104	201	202	301	302	401	501	601	701
ETHANOL	0.0519374	0.0519387	0.0519387	0.051939	0.0519377	0.0664933	0.0252898	0.0249055	0.0249055	0.0266831	4.68E-03	1.76E-10	0.0788382
H2O	0.2422489	0.2422564	0.2424532	0.2532868	0.2703149	0.041516	0.0158062	0.9055797	0.9046015	3.13E-31	2.18E-14	0	0
FORMALD	5.09E-05	5.09E-05	5.19E-05	1.73E-04	0.1140194	1.77E-05	1.00E-03	7.45E-04	6.49E-05	5.22E-31	1.91E-14	0	0
METHANOL	0.459905	0.4599142	0.4594805	0.4363418	0.5199072	0.3967	0.1521057	0.0284598	0.0293988	0.2227689	2.69E-05	3.15E-04	0.6575795
CH4O2	0.0620915	0.0620891	0.0617024	0.0398449	1.30E-03	1.22E-04	3.33E-06	0.0215294	0.0242139	8.36E-31	6.90E-24	0	0
C2H6O3	0.0207635	0.0207643	0.0205625	0.010286	5.41E-18	7.94E-07	1.89E-21	1.10E-03	9.84E-04	0	0	0	0
C3H8O4	2.60E-03	2.60E-03	2.57E-03	1.15E-03	3.43E-19	2.78E-09	5.44E-24	4.56E-05	3.21E-05	0	0	0	0
C4H10O5	3.01E-04	3.01E-04	2.97E-04	1.17E-04	2.06E-20	8.94E-12	1.49E-26	1.74E-06	9.63E-07	0	0	0	0
C5H12O6	3.31E-05	3.31E-05	3.27E-05	1.15E-05	1.19E-21	2.74E-14	3.96E-29	6.32E-08	2.75E-08	0	0	0	0
C2H6O2	0.1560766	0.1560852	0.1568922	0.1995105	0.0425183	6.93E-03	6.42E-04	5.79E-03	4.01E-03	1.08E-30	5.94E-10	0	0
C3H8O3	3.82E-03	3.82E-03	3.87E-03	6.96E-03	6.44E-18	9.82E-06	2.05E-20	9.64E-05	4.26E-05	0	0	0	0
C4H10O4	1.40E-04	1.40E-04	1.43E-04	3.63E-04	2.22E-19	2.08E-08	4.49E-23	2.40E-06	6.76E-07	0	0	0	0
C5H12O5	4.78E-06	4.78E-06	4.90E-06	1.77E-05	6.81E-21	4.12E-11	8.82E-26	5.59E-08	1.00E-08	0	0	0	0
C6H14O6	1.57E-07	1.57E-07	1.62E-07	8.26E-07	1.99E-22	7.81E-14	1.60E-28	1.25E-09	1.42E-10	0	0	0	0
ME-ACETA	0	0	0	0	0	0	0	0	0	0	0	0	0
ME-FORMA	0	0	0	0	0	0	0	0	0	0	0	0	0
METHYLAL	0	0	0	0	0	0.4879241	0.805043	0.0116499	0.0116499	0.750548	1.78E-03	0.9996849	0.2635823
POLDME-2	0	0	0	0	0	2.86E-04	1.09E-04	9.81E-05	9.81E-05	1.85E-30	5.10E-03	0	0
POLDME-3	0	0	0	0	0	0	0	0	0	2.37E-30	0.9884205	0	0
POLDME-4	0	0	0	0	0	0	0	0	0	0	0	0	0

Fig. 6

Table 4.

	100	101	102	103	104	201	202	301	302	401	501	601	701
Total Flow lbmol/hr	33.07159	33.07159	33.07162	33.07567	36.86719	14.72762	28.70703	18.35134	18.34341	27.84562	0.804239	13.92283	13.92291
Total Flow Kg/h / lb/hr	453.59237 / 1000	453.580894113 / 999.9747	453.580894113 / 999.9747	453.5781271996 / 999.9686	453.5894216496 / 999.9935	294.833135412 / 649.9958	775.1889067376 / 1708.999	158.7586902771 / 350.003	158.7587356363 / 350.0031	726.1152016197 / 1600.81	49.0737956364 / 108.1692	480.3556806071 / 1059.003	245.7567089399 / 541.8008
Total Flow cuft/hr	17.81496	17.81495	17.81961	18.22397	11892.76	13.68805	12285.54	6.296713	5.892457	32.12392	0.3044073	4879.519	11.54194
Temperature °C / °F	26.66/ 80	26.66 / 80	26.98722/ 80.55747	49.83389 / 121.701	148.8889 / 300	77.40761 / 171.3337	110.00/ 230	110.2396 / 230.4313	52.61328 / 126.7039	52.29450 / 126.1301	228.0572 / 442.5029	46.56778 / 115.822	67.26722 / 153.081
Pressure Pa / psia	1.034213592E+05/ 15	1.034213592E+05 / 15	4.826330095999995E+05/ 70	4.826330095999995E+05 / 70	1.7236893199999999E+05 / 25	1.723689319999999E+05 / 25	1.1721087376 E+05/ 17	1.7926368927999998E+05 / 26	4.2747495136E+05/ 62	1.3789514559999998E+05 / 20	1.3789514559999998E+05 / 20	1.1721087376 E+05/ 17	1.1721087376E+05/ 17
Vapor Frac	0	0	0	0	1	0	1	0	0	0	0	1	0
Liquid Frac	1	1	1	1	0	1	0	1	1	1	1	0	1
Solid Frac	0	0	0	0	0	0	0	0	0	0	0	0	0
Enthalpy Btu/lbmol	-1,23E+05	-1,23E+05	-1,23E+05	-1,22E+05	-89478.75	-1,21E+05	-1,25E+05	-1,21E+05	-1,23E+05	-1,35E+05	-3,66E+05	-1,49E+05	-1,10E+05
Enthalpy Btu/lb	-4064.78	-4064.882	-4064.268	-4027.895	-3296.851	-2731.264	-2095.846	-6320.062	-6424.051	-2354.916	-2723.037	-1957.448	-2823.565
Enthalpy Btu/hr	-4,06E+06	-4.06E+06	-4,06E+06	-4,03E+06	-3,30E+06	-1,78E+06	-3,58E+06	-2,21E+06	-2,25E+06	-3,77E+06	-2,95E+05	-2,07E+06	-1,53E+06
Entropy Btu/lbmol-R	-54.33645	-54.33632	-54.29037	-51.19703	-16.34701	-66.42007	-66.23787	-35.59661	-38.73861	-89.71354	-208.8921	-96.43142	-62.93232
Entropy Btu/lb-R	-1.796993	-1.797034	-1.795516	-1.693429	-0.6026722	-1.550263	-1.112635	-1.86641	-2.030263	-1.560552	-1.552828	-1.267794	-1.617202
Density lbmol/cuft	1.856394	1.856395	1.855911	1.814954	0.0031	1.075947	0.00234	2.914432	3.113033	0.8668252	2.641984	0.00285	1.206289
Density lb/cuft	56.13259	56.13121	56.11653	54.87107	0.0840841	47.48635	0.1391066	55.58503	59.39849	49.83235	355.4094	0.2170302	46.94192
Average MW	30.23744	30.23667	30.23664	30.23276	27.12421	44.13448	59.53243	19.07234	19.06059	57.48835	134.5237	76.06237	38.91434
Liq Vol 60F cuft/hr	17.92294	17.92291	17.91968	17.73777	18.89509	12.52655	32.41673	5.72116	5.725146	30.59671	1.602796	19.86928	10.72731
*** ALL PHASES ***													
Temperature F	80	80	80.55747	121.701	300	171.3337	230	230.4313	126.7039	126.1301	442.5029	115.822	153.081
*** VAPOR PHASE ***													
MUMX lb/ft-hr					0.0351747		0.0276147					0.021596	
MASSRHOM lb/cuft					0.0840841		0.1391066					0.2170302	
KMX Btu/hr-ft-F					0.0164133		0.0125253					0.00853	
Average MW					27.12421		59.53243					76.06237	
Enthalpy Btu/lb					-3296.851		-2095.846					-1957.448	
*** LIQUID_1 PHASE *													

FIG. 7

UPGRADING OF A RAW BLEND INTO A DIESEL FUEL SUBSTITUTE: POLY(DIMETHOXYMETHANE)

TECHNICAL FIELD

[0001] In at least one aspect, the present invention is related to a method and systems for producing poly(dimethoxymethane) from a raw blend that includes formaldehyde and methanol.

BACKGROUND

[0002] Polyoxymethylene dimethyl ethers, also referred to as Poly(dimethoxymethane), can be synthesized to present properties compatible with those of conventional diesel fuel. It has the chemical structure of $CH_3–O–(CH_2–O)_n–CH_3$. Poly(dimethoxymethane) with n=1 is dimethoxymethane (DMM), which although it has attractive properties for fuels applications, when n ranges from 3 to 5 the poly(dimethoxymethane) can be blended directly into diesel with no need for engine modifications. Furthermore, because there are no carbon-carbon bonds in the poly(dimethoxymethane) molecule, the fuel burns clean without the generation of soot.

[0003] Poly(dimethoxymethane) can be synthesized from methanol and formaldehyde as depicted from the following equation:

$$CH_3OH + n\ CH_2O \leftrightarrow CH_3O(CH_2O)_nCH_2$$

$$CH_3O(CH_2O)_2CH_2 + n\ CH_2O \leftrightarrow CH_3O(CH_2O)_{2+n}CH_2$$

For initial dimethoxymethane synthesis or further production of poly(dimethoxymethane), it is necessary to understand the dynamics of formaldehyde in solution. Formaldehyde readily reacts with water and methanol to produce methylene glycol ($HOCH_2OH$, MG), poly(oxymethylene) glycols ($H(OCH_2)_nOH$, MG_n, $n>1$), hemiformal ($HOCH_2OCH_3$, HF), and poly(oxymethylene) hemiformals ($H(OCH_2)_nOCH_3$, HF_n, $n>1$). The model presented for poly(dimethoxymethane) production takes into consideration the equilibrium conditions for formaldehyde and its availability for the dimethoxymethane synthesis reaction. Although processes for forming poly(dimethoxymethane) are known, the costs of synthesis can be unreasonably high thereby inhibiting its application in products such as diesel fuel.

[0004] Accordingly, there is a need for improved methods and systems for producing poly(dimethoxymethane).

SUMMARY

[0005] The present invention solves one or more problems of the prior art by providing in at least one embodiment, a method for forming poly(dimethoxymethane). The method includes a step of separating a formaldehyde-containing blend into a first bottom stream and a first top stream. The first formaldehyde-containing blend includes methanol, formaldehyde, and water while the first bottom stream includes water. The first top stream includes dimethoxymethane that is produced from the reaction between methanol and formaldehyde. The first top stream is separated into a second bottom stream and a second top stream. The second bottom stream includes poly(dimethoxymethane) while the second top stream includes dimethoxymethane, methanol, and ethanol. The second top stream is separated into a third bottom stream and a third top stream. The third bottom stream includes methanol and ethanol while the third top stream includes dimethoxymethane. The third top steam can be recycled to form additional poly(dimethoxymethane).

[0006] In another embodiment, a system for forming poly(dimethoxymethane) using the method set forth above is provided. The system includes a first separation station that receives a formaldehyde-containing blend and outputs a first bottom stream and a first top stream. The formaldehyde-containing blend includes methanol, formaldehyde, and water. The first top stream includes dimethoxymethane that is produced from the reaction between methanol and formaldehyde as well as unreacted methanol and formaldehyde, while the bottom stream includes water. A second separation station receives the first top stream and outputs a second bottom stream and a second top stream. The second bottom stream includes poly(dimethoxymethane) while the second top stream including dimethoxymethane, methanol, and ethanol. A third separation station receives the second top stream and outputs a third bottom stream and a third top stream. The third bottom stream includes methanol and ethanol and the third top stream including dimethoxymethane.

[0007] In another embodiment, a natural gas liquids plant is provided. The natural gas liquids plant includes a natural gas compressor that receives that receives and compresses natural gas to a pressure of 5860543,688 Pa to 7584233,007999999 (850 to 1100 psig). The natural gas compressor includes a cooler that cools the natural gas after compression to provide a compressed rich gas stream containing 5% or more C3-8 hydrocarbons. A methanol source from which methanol is injected into the compressed rich gas stream. A plurality of heat transfer units to cool the compressed rich gas stream to a sufficient temperature for separation of propane and higher hydrocarbons. The plurality of heat transfer units includes a first heat exchanger that to initially cool the rich gas stream to a first cooled stream, a second heat exchanger that cools the first cooled stream to a second cooled stream, and a third heat exchanger that cools the second cooled stream to a third cooled gas stream. The natural gas liquids plant also includes a vapor-liquid-liquid separator, a vapor-liquid separator, and an NGL stabilization column. The vapor-liquid-liquid separator separates the third cooled gas stream into a first three-phase separated vapor stream and a first three-phase separated liquid stream including water and methanol and a second three-phase separated liquid stream including natural gas liquids. The vapor-liquid separator separates the first three-phase separated vapor stream into a second two-phase separated vapor stream and a second two-phase separated liquid stream. The stabilization column separates the second two-phase separated liquid stream into a stabilization column separated vapor stream and a stabilization column separated liquid stream. Characteristically, the stabilization column separated liquid stream includes greater than 50% C3+ hydrocarbons.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIGURE 1 is a schematic illustration of a system for forming poly(dimethoxymethane).

[0009] FIGURE 2 is a schematic illustration of a system for forming gas-to-liquids (GTL).

[0010] FIGURE 3 is a schematic illustration of a high-pressure natural gas liquids (NGL) plant.

[0011] FIGURE 4 provides Table 1 showing values of the mole fraction at specified regions of the system of Figure 2.

[0012] FIGURE 5 provides Table 2 showing values of the mass flow at specified regions of the system of Figure 2.

[0013] FIGURE 6 provides Table 3 showing values of the mass fraction at specified regions of the system of Figure 2.

[0014] FIGURE 7 provides Table 4 showing values of various properties at specified regions of the system of Figure 2.

DETAILED DESCRIPTION

[0015] As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention that may be embodied in various and alternative forms. The figures are not necessarily to scale; some features may be exaggerated or minimized to show details of particular components. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for teaching one skilled in the art to variously employ the present invention.

[0016] As used herein "poly(dimethoxymethane)" without a subscript refers polyoxymethylene dimethyl ethers which can be formed from methanol and formaldehyde. In a variation, poly(dimethoxymethane) has the following formula:

$$CH_3-O-\left(CH_2-O\right)_n-CH_3$$

where n is 2 to 8 (i.e., 2, 3, 4, 5, 6, 7, 8). This formula can also be expressed as poly(dimethoxymethane)$_n$. In a refinement, n is 3 to 8. In still another refinement, n is 3 to 5.

[0017] As used herein "top stream" means the relatively volatile components compared to the "bottom stream" that are removed in a separation station.

[0018] As used herein “bottom stream” means the less volatile components compared to the “top stream” that are removed in a separation station. In a separation column, the top stream exits at the top of the column while the bottom stream exits at the bottom of the column.

[0019] With reference to Figure 1, a schematic illustration of a system for forming poly(dimethoxymethane) is provided. System **10** includes source **12** of a formaldehyde-containing blend **14** that is provided to a first separation station **18** via pump **13**. Heat exchanger **16** can optionally be used to recover heat from the first bottom stream **20** to heat the formaldehyde-containing blend **14**. In a refinement, heater **19** is used to heat formaldehyde-containing blend **14** to form heated formaldehyde-containing blend **14’**. The heated formaldehyde-containing blend is found at a temperature near the boiling point of the stream, in the range of 250 to 275 F. The high temperatures facilitate breakdown of poly(oxymethylene) glycols and poly(oxymethylene) hemiformals into the simple components of formaldehyde, methanol, water and shorter oligomers. First separation station **18** outputs first bottom stream **20** and first top stream **22**. Formaldehyde-containing blend **14** includes methanol, formaldehyde, and water. First bottom stream **20** includes water (e.g. 30-100 mole percent). First top stream **22** includes dimethoxymethane that is produced from the reaction between methanol and formaldehyde. In a refinement, first separation station **18** is performed by reactive distillation. Details for reactive distillation are set forth in U.S. Pat. Pub. No. 20170081602; the entire disclosure of which is hereby incorporated by reference. In general, reactive distillation uses a catalyst-packed column having a catalyst that converts alcohols to ethers and/or ketones and aldehydes. When reactive distillation is deployed, operating pressures are typically between 0 and 1723689,32 Pa (0 and 250 psia), preferably between 101352.9320 and 1034213.5920 Pa (14.7 and 150 psi). In a refinement, the catalyst is an immobilized catalyst. Examples of such catalysts include, but are not limited to, aluminosilicate catalysts, copper modified alumina catalyst, combinations thereof and the like. At these elevated pressures the boiling point of methanol is increased to the preferred temperatures for alcohol dehydration, between 50 and 300 ^{o}C, and preferably between 150 and 250 ^{o}C.

[0020] In a refinement, the heat from the first bottom stream can be transferred to the formaldehyde-containing stream **14**. In a refinement, heater **26** can be used to heat first top stream **22** to form heated top stream **22’**. First top stream **22’** is introduced into second separation station **30** that outputs second bottom stream **32** and a second top stream **34**. Second bottom stream **32** includes poly(dimethoxymethane) while second top stream **34** including dimethoxymethane. Second top stream **34** is introduced into a third separation station **40** that outputs a third bottom stream **42** and third top stream **44**. Third bottom stream **42** includes methanol and ethanol while the third top stream **44** includes dimethoxymethane.

[0021] In a variation, formaldehyde-containing blend **14** includes up to 40 mole % water. In a refinement, formaldehyde-containing blend **14** includes from 5 to 30 mole % water. Moreover, the first feed stream can also include methylal, methanol, ethanol, formaldehyde and its derivatives in solution, as well as minor concentrations of higher alcohols (e.g. propanol) and weak acids (e.g. formic acid, acetic acid).

[0022] In another variation, the first separation station **18** includes and/or is a first separation column **50**. In a refinement, the first separation column including an acid catalyst that promotes acetylation. Examples of such catalysts include, but are not limited to, aluminosilicate catalysts, copper modified alumina catalyst, sulfonic acid ion exchange resins, ionic liquids and combinations thereof and the like. Operating temperatures and pressures range from 103421,35919999999- 206842,71839999998 Pa (15-30 psig) and 76,67- 121,11°C (170-250 °F).

[0023] In a variation, second separation station **30** includes and/or is a second separation column **52**. In a refinement, second separation station **30** includes an acid catalyst that accelerates equilibrium between DMM-formaldehyde-methanol. Examples of such catalysts include, but are not limited to, aluminosilicate catalysts, copper modified alumina catalysts, sulfonic acid ion exchange resins, ionic liquids and combinations thereof and the like. In a further refinement, the acid catalyst also promotes reaction between dimethoxymethane, poly(dimethoxymethane), and formaldehyde to produce

$$CH_3-O-\left(CH_2-O\right)_n-CH_3$$

[0024]with n=3-5. Acquisition of poly(DMM) in the desired boiling range, e.g. n=3-5, is controlled by the column temperature. Furthermore, the presence of water tends to reduce selectivity to poly(DMM) in the n=3-5 range and increase selectivity of poly$(DMM)_2$, therefore by removing nearly all water in the first separation station the present process maximizes synthesis of poly(DMM)$_{3-5}$. Unreacted light components such as DMM and poly(DMM)$_2$ can be recycled for their upgrade to poly(DMM)$_{3-5}$. In a further refinement, second separation station 30 includes a catalytic reaction vessel followed by a distillation column. The same catalyst can be used for both the synthesis of DMM as well as Poly(DMM), therefore the catalysts of potential application in separation 30 include, but are not limited to, aluminosilicate catalysts, copper modified alumina catalysts, sulfonic acid ion exchange resins, ionic liquids and combinations thereof and the like.

[0025] In another variation, the second separation station **30** includes a reactor vessel containing an acid catalyst that accelerates equilibrium between DMM-formaldehyde-methanol, and also promotes reaction between dimethoxymethane, poly(dimethoxymethane), and formaldehyde to produce Poly(DMM)$_{3-5}$. The same catalyst can be used for both the synthesis of DMM as well as Poly(DMM), therefore the catalysts of potential application in separation **30** include, but are not limited to, aluminosilicate catalysts, copper modified alumina catalysts, sulfonic acid ion exchange resins, ionic liquids and combinations thereof and the like. Both variations of separation station 30 operate at low pressure (34473,7864- 172368,932 Pa / 5-25 psig) and temperatures in the range of 51,66 to 148,89°C (125 to 300 °F).

[0026] In a variation, the third separation station **40** is a distillation column **54** in which dimethoxymethane is separated from the alcohols methanol and ethanol. This separation station operates at near ambient pressure (34473,7864- 68947,5728 Pa / 5-10 psig) and temperatures ranging from 43,33 to 79,44 °C. (110 to 175 °F).

[0027] The system of Figure 1 can use many types of blends of hydrocarbon liquids with partial oxygenates thereof as a feedstock. In some variations, the feedstock is the product of a gas-to-liquids process which is understood to include processes that converts methane and/or blends of C_{1-4} alkanes into longer hydrocarbon chains (e.g., C_{5-10} alkanes) with partial oxygenates of C_{1-4} alkanes (formaldehyde, aldehydes, ketones, alcohols, and the like). With reference to Figure 2, a schematic illustration of a gas-to-liquids (GTL) system of U.S. Pat. No. 9,255,051 that can be provide the gas blend introduced into the system of Figure 1. The entire disclosure of U.S. Pat. No. 9,255,051 that is hereby incorporated by reference in its entirety. Homogeneous direct partial oxidation is performed in a reactor **60** which is supplied with a hydrocarbon-containing gas **62** and an oxygen-containing gas **64**. In a refinement, the reaction is operated at pressures from about 3102640,776 to 8618446,6 Pa (450 to 1250 psia) and temperatures from about 350 to 450° C. In particular, hydrocarbon-containing gas **62** and an oxygen-containing gas **64** react in a vessel to form a first product blend which is a blend (i.e., a mixture) of partially oxygenated compounds that include formaldehyde. In a refinement, the first product blend and/or output streams **66**, **68** include C_{1-10} alcohols and/or C_{1-5}aldehydes. In another refinement, the first product blend and/or output streams **66**, **68** include an alcohol selected from the group consisting of methanol, ethanol, propanols (n-propyl alcohol, isopranol), butanols (n-butanol, sec-butanol, t-butanol, isobutanol), pentanols (n-pentanol, isopentanol, sec-pentanol, etc) and combinations thereof, and/or aldehyde selected from the group consisting formaldehyde, acetaldehyde, propionaldehyde and combinations thereof. In another refinement, the first product blend and/or output streams **66**, **68** include an alcohol selected from the group consisting of methanol, ethanol, and combinations thereof, and aldehyde selected from the group consisting formaldehyde, acetaldehyde, and combinations thereof. Examples of systems and methods of performing the partial oxidation as set forth in U.S. Pat. Nos. 8,293,186; 8,202,916; 8,193,254; 7,910,787; 7,687,669; 7,642,293; 7,879,296; 7,456,327; and 7,578,981; the entire disclosures of which are hereby incorporated by reference. In a refinement, the hydrocarbon-containing gas includes C_{1-10} alkanes. In another refinement, the hydrocarbon-containing gas includes an alkane selected from the group consisting of methane, ethane, propanes, butanes, pentanes and combinations thereof. In another refinement, the hydrocarbon-containing gas includes an alkane selected from the group consisting of methane, ethane, and combinations thereof. Examples of oxygen containing gas include molecular oxygen which may be in the form of concentrated oxygen or air. In a refinement, the oxygen-containing gas stream is made oxygen rich (e.g., by passing air through a membrane to increase oxygen content). The low conversion and selectivity of homogeneous direct partial oxidation requires that a recycle loop is utilized to increase the overall carbon efficiency.

[0028] Following partial oxidation reaction the reactant stream is rapidly cooled in a series of heat exchangers **70** and **74** to prevent decomposition of the produced oxygenates. The heat energy transferred by exchanger **74** might optionally be used to provide energy which may be used in the creation of synthesis gas or to drive downstream distillation processes. After cooling the liquids are separated from the gas stream as station **76**. The gas stream is then submitted to a separation process for removal of non-hydrocarbon fractions a station **78** which may be performed via scrubbing, membrane separation, adsorption processes, cryogenic separations, or by purging a small gas fraction. If station **78** is a liquid scrubbing system, liquid products are sent to a flash drum **80** where dissolved gases are removed. Non-hydrocarbon gases 82 are removed from the recycle loop **84**, and the hydrocarbon gases **86** are then recycled to combine with fresh methane gas **90** which has been pressurized to the pressure of the loop by compressor **92**. The stream composed of recycled hydrocarbons plus fresh methane gas is pressurized to make up for pressure losses in the recycle loop, preheated via the cross exchanger **70** and further by the preheater **96**, when necessary, to meet the desired reaction conditions.

[0029] Liquids generated by the gas-to-chemicals process are composed predominantly of alcohols and aldehydes (e.g., methanol, ethanol and formaldehyde) as set forth above. The raw liquid stream **97** generated by the GTL process is generally composed of 40-70 mole % alcohols and 5-20 mole % aldehydes 15-40 mole % water. Downstream processing of these liquids may include a number of different synthesis routes to higher-value chemicals and fuels, but simple distillation of alcohols from aldehydes is performed in a simple fractional distillation column **98** in which alcohols are recovered in the distillate **66** and the aqueous aldehyde solution from the column bottoms **68**.

[0030] Figure 3 provides a schematic illustration of a high-pressure natural gas liquids (NGL) plant **100** designed with the intent of utilizing the Joules Thompson expansion effect for cooling of rich natural gas for separation of natural gas liquids while also producing a high-pressure lean gas suitable for application in a GTL process. The produced NGL's are dropped from high pressure to the NGL storage pressure and the chilled NGL's are used to remove heat from the incoming raw gas stream, furthermore, an additional portion of the lean gas and that off the top of the stabilization column can be recycled to the compressor suction and also used to remove heat from the incoming raw gas.

[0031] With reference to Figure 3, a Btu-rich natural gas stream containing 5% or more of C3-8 hydrocarbons **105** is first fed to a natural gas compressor **106** where it is compressed to

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an operating pressure of 5860543,688 - 7584233,007999999 Pa (850-1100 psig). Following compression, the natural gas flows through the aftercooler of the same compressor **106** so that it reaches a final temperature of approximately ambient -12,22°C (+ 10°F). Methanol from methanol source **107** is then injected into the gas stream **114** at the concentration required to inhibit natural gas hydrate formation. This methanol source may be external or generated by the local gas-to-methanol conversion process.

[0032] After this, the gas enters a series of heat transfer units until reaching temperatures adequate for separation of propane and higher hydrocarbons. The first heat exchange unit **108** utilizes the cold lean (from which approximately 80% of C3-8 hydrocarbons have been removed) gas stream **110** exiting the vapor-liquid-liquid separator **112** (i.e., a three phase separator) to initially chill the compressed rich gas **114**. Details vapor-liquid separators is found in Cusack R. et al. Hydrocarbon Processing, June 2009, pgs 53-60; the entire disclosure of which is hereby incorporated by reference.

[0033] This initially cooled natural gas stream **116** is further cooled in the second heat exchange unit **118** with heat being exchanged via heat transfer to cooling gas 128. The cooling gas **128** is composed of the vapor stream **126** exiting the vapor-liquid separator **124** (i.e., a two-phase separator) and the vapor steam **122** exiting the top of the stabilization column **128**. Additionally, in order to meet the overall cooling requirements, a specific portion of the high-pressure lean gas **130** (from which approximately 80% of C3-8 hydrocarbons have been removed) exiting the first heat exchanger unit **108** can be submitted to a pressure drop via a control valve **201** which generates an isenthalpic expansion process also known as Joule-Thomson cooling, and blended into stream **128** to provide additional cooling of the raw rich gas **116** (containing all natural gas liquids as in the initial gas stream **105**).

[0034] The final heat exchange unit **132** further cools the rich gas **134** (containing all natural gas liquids as in the initial gas stream **105**) by transferring heat from the super-cooled NGL liquid stream **136**. This unit operation cools the incoming gas to the final separation conditions of approximately 4.444°C (40 °F) at approximately 7584233.0083Pa (1100 psi). This cooled rich gas rich in natural gas liquids (C3-8 hydrocarbons) **138** then enters a vapor-liquid-

liquid separator **112** in which the liquids and gas are separated and the two liquids phases (NGL and water/methanol) also separate.

[0035] The obtained NGL stream **136** is submitted to a pressure drop, via a control valve **202** which generates an isenthalpic expansion process to approximately 1034213.5920 Pa (150 psi) which results in an extreme cooling effect, making it especially effective to cool the incoming natural gas liquids-rich stream. However, after exiting the final heat exchanger unit **132**, some of the light hydrocarbons boil to the vapor phase and therefore need to be separated from the liquids in a simple vapor-liquid separator **124**. In this regard, vapor phase stream 137 is provided to the vapor-liquid separator 124. Exiting the vapor-liquid separator **124** is a relatively rich gas stream with high propane concentration (e.g. approximately 1400 btu/scf) **126** and a stable liquid NGL stream **142**.

[0036] A final separation column, e.g. NGL stabilization column, **128** is utilized to reduce ethane concentrations in the NGL stream while retaining the maximum concentration of C3-8 hydrocarbons. The stabilized liquid stream **146** can optionally be further cooled to ensure its stable storage.

[0037] The vapor stream **122** exiting the top of the separation column can also contain up to 20% C3-C8 hydrocarbons and is combined with the vapor stream exiting the vapor-liquid separator **126** to be recycled to the suction side **149** of the compressor **106** as vapor stream **150**. Because stream **150** contains a significant amount of propane, by recycling this steam the overall propane recover can be greatly improved, increasing overall propane recovery values to greater than 75%.

[0038] The NGL separation column **128** requires a heat source to act as a reboiler for separating the light components (ethane) from the heavy components (propane). This can be accomplished by using a simple electric heater, or via heat integration, where the heat generated by the compressor or the GTL system can be utilized to provide heat to the reboiler.

[0039] Figures 4-7 provides tables giving values of reaction parameters at position labeled in Figure 1 used in a thermokinetic model of the reactor. The process model was devoled considering the formaldehyde-water-methanol equilibrium data published by Maurer (1986) and component properties derived from the UNIFAC method. Synthesis of poly(DMM) was based on equilibrium conditions based on Gibbs free energy. Table 1 provides the mole fraction for each stream in the system of Figure 1. First bottom stream **20** includes composition **301** while first top stream **22** includes composition **201** and heat first top stream **22'** includes composition **202**. Second bottom stream **32** includes composition **501** while second top stream **34** includes composition **401**. Third bottom stream **42** includes composition **701** while third top stream **44** includes composition **601**. The composition provided to system **10** includes composition **101**, the composition after pump **13** includes composition **102**. The composition after pump **19** includes composition **103**. The composition between heat **19** and first separation station **18** includes composition **104**. The composition recycled from and first separation station **18** to pump **16** includes composition **301**. Figure 5 provides Table 2 showing values of the mass flow at specified regions of the system of Figure 1. Figure 6 provides Table 3 showing values of the mass fraction at specified regions of the system of Figure 1. Figure 7 provides Table 4 showing values of various properties at specified regions of the system of Figure 1. In various embodiments of the systems of Figure 1, the values in Tables 1-4 can vary within a range of +/- 30 percent of the indicated value with the understanding that percentages will be truncated at 0 or 100 percent when applicable and fractions will be truncated at 0 and 1 when applicable.

[0040] While exemplary embodiments are described above, it is not intended that these embodiments describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention. Additionally, the features of various implementing embodiments may be combined to form further embodiments of the invention.

CLAIMS

1. A method for producing polyoxymethylene dimethyl ethers from a blend that includes formaldehyde, ethanol, water and methanol, said method comprising:

a) subjecting said blend to a reactive distillation to synthesize dimethoxymethane by reacting methanol and formaldehyde of said blend and separating the reacted blend into a first bottom stream and a first top stream, said first top stream including dimethoxymethane and , said first bottom stream including water;

b) synthesizing polyoxymethylene dimethyl ethers by subjecting said first top stream to a further reactive distillation and separating said reacted first top stream into a second bottom stream and a second top stream, said second bottom stream comprising said polyoxymethylene dimethyl ethers and said second top stream including unreacted dimethoxymethane, methanol and ethanol; and

c) separating through distillation said second top stream into a third bottom stream and a third top stream, said third bottom stream including methanol and ethanol while said third top stream comprises said unreacted dimethoxymethane.

2. The method of claim 1 wherein said blend is composed of at least 40-70 mole % alcohols, 5-20 mole % aldehydes and 15-40 mole % water

3. The method of claim 1 wherein said third top stream is further recycled to form additional polyoxymethylene dimethyl ethers.

4. The method of claim 1 wherein said blend includes up to 30 mole % water.

5. The method of claim 1 wherein said first top stream includes methylal, methanol, ethanol and unreacted formaldehyde

6. The method of claim 1 wherein step a) is performed in the presence of an acid catalyst that promotes acetylation.

7. The method of claim 1 wherein step b) is performed in the presence of an acid catalyst that accelerates equilibrium between dimethoxymethane, formaldehyde, and methanol

8. The method of claim 7 wherein said acid catalyst also promotes reaction between dimethoxymethane, polyoxymethylene dimethyl ethers , and formaldehyde to produced poly(dimethoxymethane)$_n$ with n=3-5.

9. A system when used in the method according to claim 1, said system comprising:

a first reaction and separation station comprising a first distillation column that receives a formaldehyde-containing blend and outputs a first bottom stream and a first top stream, the formaldehyde-containing blend including methanol, ethanol, formaldehyde, and water, the first top stream including dimethoxymethane that is produced from a reaction between methanol and formaldehyde, the first bottom stream including water;

a second reaction and separation station comprising a second distillation column that receives the first top stream and outputs a second bottom stream and a second top stream, the second bottom stream including poly(dimethoxymethane) and the second top stream including dimethoxymethane, methanol and ethanol; and

a third separation station constituted of at third separation column that receives the second top stream and outputs a third bottom stream and a third top stream, the third bottom stream including methanol and ethanol and the third top stream including dimethoxymethane.

10 The system of claim 9 further comprising a recycle loop that recycles dimethoxymethane from the third separation station back to the second separation station.

11. The system of claim 9 wherein said first distillation column includes an acid catalyst that promotes acetylation.

12. The system of claim 9 wherein said second separation station includes an acid catalyst that accelerates equilibrium between dimethoxymethane, formaldehyde, and methanol.

13. The system of claim 9 wherein said second separation station includes a catalytic reaction vessel followed by a distillation column.

14. The system of claim 13 wherein said catalytic reaction vessel comprises an acid catalyst that promotes reaction between dimethoxymethane, polyoxymethylene dimethyl ethers , and formaldehyde to produced poly(dimethoxymethane)$_n$ with n=3-5.

15. A system according to claim 9, further comprising before said first reaction and separation station :

a natural gas compressor that receives and compresses natural gas to a pressure of 850 to 1100 psig, said natural gas compressor including a cooler that cools the natural gas after compression;

a methanol source for injecting methanol in said compressed gas thus forming a rich gas stream ;

a plurality of heat transfer units that cool the compressed rich gas stream to a sufficient temperature for separation of propane and higher hydrocarbons, the plurality of heat transfer units including:

a first heat exchanger to initially cool the compressed rich gas stream to a first cooled stream;

a second heat exchanger that cools the first cooled stream to a second cooled stream; and

a third heat exchanger that cools the second cooled stream to a third cooled gas stream,

a vapor-liquid-liquid separator that separates the third cooled gas stream into a first three-phase separated vapor stream, a first three-phase separated liquid stream including water and methanol and a second three-phase separated liquid stream including natural gas liquid;

a vapor-liquid separator that separates the first three-phase separated vapor stream into a second two-phase separated vapor stream and a second two-phase separated liquid stream; and

a stabilization column for separating said second two-phase separated liquid stream into a stabilization column separated vapor stream and a stabilization column separated liquid stream,

16. The system according to claim 9, wherein said vapor-liquid separator vapor exit is connected to the exit of said stabilization column and wherein it further comprises a pipe connected to said second heat exchanger to provide the mixture of said vapor stream exiting said vapor-liquid separator and said stabilization column separated vapor stream exiting said stabilization column, as a cooling gas to said second heat exchanger.

17. The system according to claim 9 wherein it further comprises a control valve which generates an isenthalpic expansion process of a portion of the high-pressure lean gas exiting the first heat exchanger and blends said cooled portion of said high-pressure lean gas with the stream entering said second heat exchange unit to provide additional cooling of said first cooled stream .

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18. The system according of claim 9wherein said the exit of the vapor-liquid-liquid separator is connected to said third heat exchanger for cooling said second cooled stream.

19. The system of claim 9 wherein the exit of said vapor exit of said vapor-liquid-liquid separator is connected to said first heat exchanger to cool said compressed rich gas stream.

20. The system of claim 9 wherein the exit of stabilization column is connected to the exit of said two-phase separator and wherein it further comprises a pipe for recycling the combination of said stabilization column vapor stream and said second two phase separated vapor stream to a suction side of said natural gas compressor.

21. The system of claim further comprising a heat source in communication with said stabilization column to act as a reboiler for separating light components from heavy components.