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Process Intensification of Dimethyl Ether using Aspen HYSYS

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***Abstract*: Dimethyl Ether (DME) is a precursor to many organic compounds and is currently used as an aerosol propellant. Its market growth rate has been about 19.65% annually up to 2020 and the presence of production facilities of DME in India have been non-existent till 2016 and the situation has remained quite same even today. With the process intensification changes proposed, DME production can be easily sustained. First, the proposed process makes use of natural gas, which is abundant in India (reserves equivalent to 22.1 times its annual consumption) to produce synthesis gas through unit processes and operations, in turn leading to cost effectiveness. Next, the proposed process makes use of process lines as utilities (thereby reducing energy consumption to almost nil). Also, the process has successfully conducted dehydration of methanol at relatively lower temperatures using Aspen HYSYS. All these suggested alterations prove to be a game changer for DME production in India, which is expected to have a humongous demand domestically as a clean fuel in the future.**

***Keywords*: Process Intensification; Dimethyl Ether; Natural Gas; Aspen HYSYS.**

1. Introduction

Dimethyl ether (IUPAC: methoxymethane, molar weight: 46 g/mol), the simplest ether, is a colorless gas under ambient conditions. It is instrumental in to produce different chemicals and as an aerosol propellant. It has been found that DME is found in abundance in hot cores, the dense and warm regions of molecular clouds where massive stars are forming. Usually, it is synthesized by dehydration of methanol. DME has a high cetane number, DME can be used in diesel engines as a substitute for conventional diesel fuel due to its good ignition quality. However, compared to diesel fuel DME has a lower viscosity (insufficient), and poor lubricity. Like LPG for gasoline engines, DME is stored in the liquid state under relatively low pressure of 0.5 MPa. DME in diesel engine burns very cleanly with no soot. The global dimethyl Ether market is projected to account for 15 billion USD in terms of value by the end of 2027, witnessing a CAGR of 9.5% during the forecast period (2020-2027) [1]. Exponential increase in the adoption of DME is expected to propel growth of the global dimethyl ether market over the forecast period, for which, a sustainable method of production is needed on multiple fronts, which is discussed in this paper.

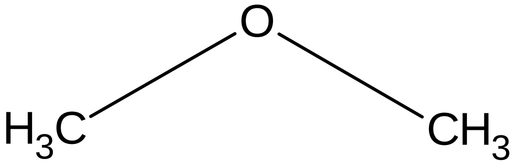

Fig. 1. Structure of DME

2. Existing Method of Production

Fixed-bed catalytic dehydration of methanol is done to produce DME. In vintage times until 1975, DME was produced as a by-product (3-5 wt. %) during methanol synthesis at high pressures. The new low pressure methanol synthesis route was developed then which does not give DME as a by-product, so for mass production this method is followed widely.

Description (refer fig. 2):

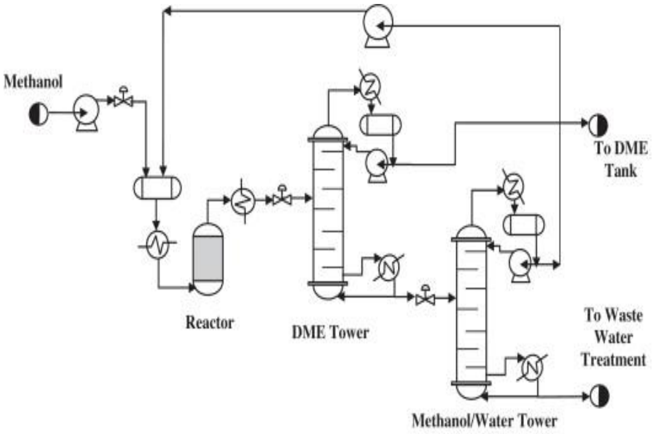

Fig. 2. Conventional Process

In conventional DME production by dehydration of methanol, the feed is pumped at about a pressure of 10 to 12 atm and is blended with recycled methanol before it is

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*Corresponding author: jainmihir0108@gmail.com evaporated in the reactor. The dehydration reaction is conducted in an adiabatic reactor loaded with a dehydration catalyst. The operating temperature range is of the order of 290-400 °C with almost 80% conversion of methanol. The reactor effluent is cooled off and the DME is separated from methanol and water from which methanol is sent back to the dehydration reactor. The catalysts used are based on γ alumina or silica alumina (acidic) [2].

A. *Suggested Modification*

a) The conventional method makes use of methanol as the raw material in most of the cases, however, there are two major issues with storing and transporting it:

1. Combustion
2. Corrosion

1) *Combustion*

The most extensively recognized hazard associated with methanol is combustion. Ignition and sustained combustion occur in the vapor phase immediately above a liquid surface: vapors burn; liquids do not. Conditions capable of supporting combustion are determined by the partial pressure of methanol vapor above a liquid, and the relative molar concentration of methanol vapor in surrounding air. Methanol vapor/air mixtures with concentrations between the flammability limits will burn in a sustained manner if ignited. Ignition energy of methanol is similar to that for gasoline boiling-range fuels which increase its risk to handle [3].

2) *Corrosion*

Corrosion is a second hazard resulting from the affinity between methanol and water. Air-absorbed moisture in the presence of inorganic salts causes methanol to be unexpectedly corrosive to carbon steel alloys which are commonly used for containment. Methanol containment systems require special provisions for corrosion monitoring, crack detection around high stress welded joints, and non-destructive inspection of anomalous conditions which are subject to crevice and pitting-types of corrosion. This is true for storage, transport and piping systems. Pipelines may also be subject to accelerated localized corrosion if used to transport methanol or methanol/gasoline blends. Methanol usually contains up to 40 mg/L of dissolved oxygen at 25°C: an amount that increases corrosion rates [3]. Though natural gas has been used in isolated cases for producing DME, majority of producers don't make use of it. The proposed changes suggest use of natural gas, which is abundant in India to produce methanol via synthesis gas as a lucrative method.

Advantage: Both the factors contribute towards surge in DME production rates, which needs to be taken care of in the long run. India holds 43 trillion cubic feet (Tcf) of proven gas reserves as of 2017, ranking 22nd in the world and accounting for about 1% of the world's total natural gas reserves of 6,923 Tcf. Moreover, India has proven reserves equivalent to 22.1 times its annual consumption. Usage of the excessive natural gas would be lucrative in such a scenario, to cover up for threats posed by methanol and for a place of India where DME isn't manufactured, this method could be useful, given the fact that use of DME will burgeon in the future as a clean fuel [4] [8].

a) The suggested production method makes use of the bottom product from the 1st distillation column to cool a process stream (top product from the same distillation column) instead of a cooler. Then, the stream is further cooled using water (at 30 °C, which is abundant in India) Furthermore, the bottom product from the second distillation column is used to heat the final DME product steam to bring it to room temperature, which would make it convenient to transport. Also, before the feed enters reactor R-04, it has to be raised to a certain temperature (175 °C) which is done partially (up to 76 °C) by using the heat from an outlet water stream from HE-03.

Advantage: Substitution of coolers by heat exchangers using the energy of an in-process stream saves energy, and in turn leads to cost cutting. Transportation at room temperature won't require refrigeration and special containers, thereby proving viable.

a) The pre-existing method requires a temperature of 290- 400°C for dehydrating methanol. However, this paper has successfully managed to produce the same conversion of methanol (approximately 80%) at lower temperatures with the range of 175-200°C.

Advantage: The ability to achieve similar conversion rates at lower temperature will employ lesser heat, and thus be economical.

B. *Modified Process Description*

Chemical Reactions involved:

$$CH4 \;+\; 1/2O_2 \;\rightarrow\; CO \;+\; 2H_2$$

$$CH4 \;+\; O_2 \;\rightarrow\; CO_2 \;+\; 2H_2$$

$$CO \;+\; 2H_2 \;\leftrightarrow\; CH_3OH$$

$$CO_2 \;+\; 3H_2 \;\leftrightarrow\; CH_3OH \;+\; H_2O$$

$$2CH_3OH \;\leftrightarrow\; CH_3OCH_3 \;+\; H_2O$$

The process makes use of two feed streams of natural gas (S-01, S-02) both of different compositions, i.e., taken from two different sources) and the fluid package used to calculate all the thermodynamic properties is 'Peng Robinson' (refer fig. 3, table 1 and 2). The feed steams are fed to the 1st distillation column (DC-01) to separate methane (top product, S-03, which contains traces of N2, CO2 and C2H6) from the other hydrocarbons (C2 to C8) forming the bottom product S-04.

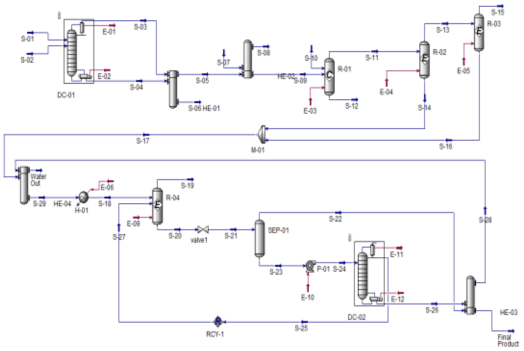
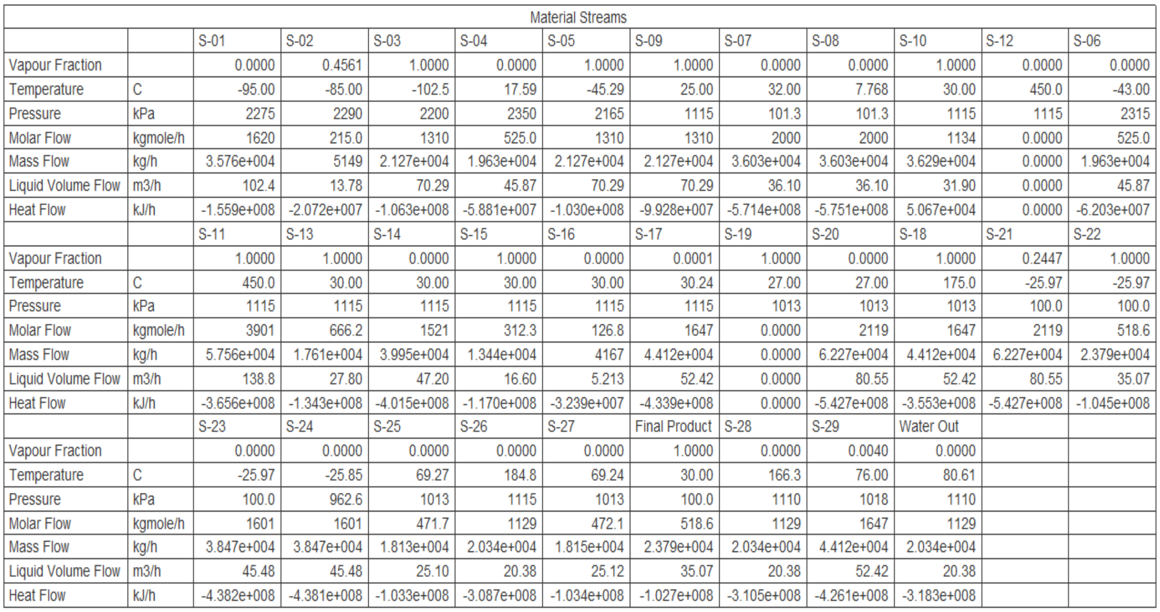


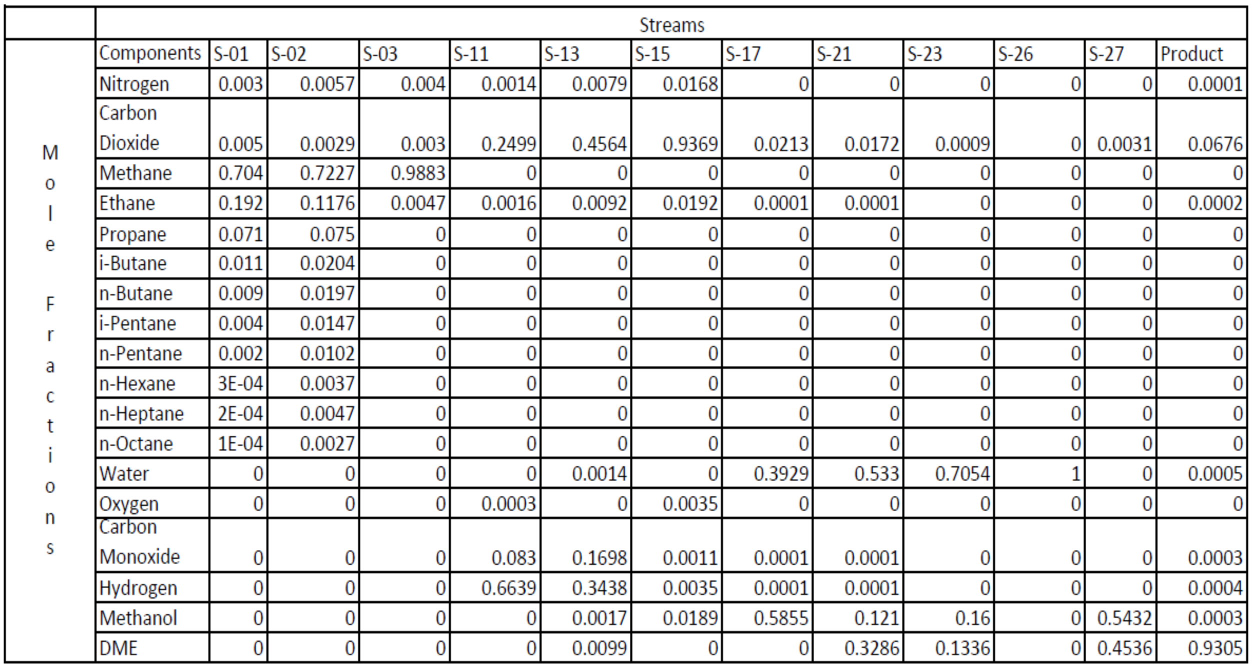
Fig. 3. Suggested process flow diagram

Table 1
Stream Details



Material Streams												
		S-01	S-02	S-03	S-04	S-05	S-09	S-07	S-08	S-10	S-12	S-06
Vapour Fraction		0.0000	0.4561	1.0000	0.0000	1.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
Temperature	C	-95.00	-85.00	-102.5	17.59	-45.29	25.00	32.00	7.768	30.00	450.0	-43.00
Pressure	kPa	2275	2290	2200	2350	2165	1115	101.3	101.3	1115	1115	2315
Molar Flow	kgmole/h	1620	215.0	1310	525.0	1310	1310	2000	2000	1134	0.0000	525.0
Mass Flow	kg/h	3.576e+004	5149	2.127e+004	1.963e+004	2.127e+004	2.127e+004	3.603e+004	3.603e+004	3.629e+004	0.0000	1.963e+004
Liquid Volume Flow	m3/h	102.4	13.78	70.29	45.87	70.29	70.29	36.10	36.10	31.90	0.0000	45.87
Heat Flow	kJ/h	-1.559e+008	-2.072e+007	-1.063e+008	-5.881e+007	-1.030e+008	-9.928e+007	-5.714e+008	-5.751e+008	5.067e+004	0.0000	-6.203e+007
		S-11	S-13	S-14	S-15	S-16	S-17	S-19	S-20	S-18	S-21	S-22
Vapour Fraction		1.0000	1.0000	0.0000	1.0000	0.0000	0.0001	1.0000	0.0000	1.0000	0.2447	1.0000
Temperature	C	450.0	30.00	30.00	30.00	30.00	30.24	27.00	27.00	175.0	-25.97	-25.97
Pressure	kPa	1115	1115	1115	1115	1115	1115	1013	1013	1013	100.0	100.0
Molar Flow	kgmole/h	3901	666.2	1521	312.3	126.8	1647	0.0000	2119	1647	2119	518.6
Mass Flow	kg/h	5.756e+004	1.761e+004	3.995e+004	1.344e+004	4167	4.412e+004	0.0000	6.227e+004	4.412e+004	6.227e+004	2.379e+004
Liquid Volume Flow	m3/h	138.8	27.80	47.20	16.60	5.213	52.42	0.0000	80.55	52.42	80.55	35.07
Heat Flow	kJ/h	-3.656e+008	-1.343e+008	-4.015e+008	-1.170e+008	-3.239e+007	-4.339e+008	0.0000	-5.427e+008	-3.553e+008	-5.427e+008	-1.045e+008
		S-23	S-24	S-25	S-26	S-27	Final Product	S-28	S-29	Water Out		
Vapour Fraction		0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0040	0.0000		
Temperature	C	-25.97	-25.85	69.27	184.8	69.24	30.00	166.3	76.00	80.61		
Pressure	kPa	100.0	962.6	1013	1115	1013	100.0	1110	1018	1110		
Molar Flow	kgmole/h	1601	1601	471.7	1129	472.1	518.6	1129	1647	1129		
Mass Flow	kg/h	3.847e+004	3.847e+004	1.813e+004	2.034e+004	1.815e+004	2.379e+004	2.034e+004	4.412e+004	2.034e+004		
Liquid Volume Flow	m3/h	45.48	45.48	25.10	20.38	25.12	35.07	20.38	52.42	20.38		
Heat Flow	kJ/h	-4.382e+008	-4.381e+008	-1.033e+008	-3.087e+008	-1.034e+008	-1.027e+008	-3.105e+008	-4.261e+008	-3.183e+008		

Table 2
Stream Compositions



	Streams												
Mole Fractions	Components	S-01	S-02	S-03	S-11	S-13	S-15	S-17	S-21	S-23	S-26	S-27	Product
	Nitrogen	0.003	0.0057	0.004	0.0014	0.0079	0.0168	0	0	0	0	0	0.0001
	Carbon Dioxide	0.005	0.0029	0.003	0.2499	0.4564	0.9369	0.0213	0.0172	0.0009	0	0.0031	0.0676
	Methane	0.704	0.7227	0.9883	0	0	0	0	0	0	0	0	0
	Ethane	0.192	0.1176	0.0047	0.0016	0.0092	0.0192	0.0001	0.0001	0	0	0	0.0002
	Propane	0.071	0.075	0	0	0	0	0	0	0	0	0	0
	i-Butane	0.011	0.0204	0	0	0	0	0	0	0	0	0	0
	n-Butane	0.009	0.0197	0	0	0	0	0	0	0	0	0	0
	i-Pentane	0.004	0.0147	0	0	0	0	0	0	0	0	0	0
	n-Pentane	0.002	0.0102	0	0	0	0	0	0	0	0	0	0
	n-Hexane	3E-04	0.0037	0	0	0	0	0	0	0	0	0	0
	n-Heptane	2E-04	0.0047	0	0	0	0	0	0	0	0	0	0
	n-Octane	1E-04	0.0027	0	0	0	0	0	0	0	0	0	0
	Water	0	0	0	0	0.0014	0	0.3929	0.533	0.7054	1	0	0.0005
	Oxygen	0	0	0	0.0003	0	0.0035	0	0	0	0	0	0
	Carbon Monoxide	0	0	0	0.083	0.1698	0.0011	0.0001	0.0001	0	0	0	0.0003
	Hydrogen	0	0	0	0.6639	0.3438	0.0035	0.0001	0.0001	0	0	0	0.0004
	Methanol	0	0	0	0	0.0017	0.0189	0.5855	0.121	0.16	0	0.5432	0.0003
	DME	0	0	0	0	0.0099	0	0	0.3286	0.1336	0	0.4536	0.9305

Table 3
DC-01

	Stage	**Pressure KPa**	**Temperature °C**	**Net Liquid kmol/hr**	**Net Vapour kmol/hr**
Condenser	0	2200	-102.5	185.6	1310.0
1__Main Tower	1	2200	-99.2	141.9	1495.6
2__Main Tower	2	2216.667	-96.2	119.6	1451.9
3__Main Tower	3	2233.333	-94.3	108.4	1429.6
4__Main Tower	4	2250	-93.2	86.7	1418.4
5__Main Tower (Entry Stage)	5	2266.667	-90.9	1728.4	1396.7
6__Main Tower	6	2283.333	-80.0	1499.4	1203.4
7__Main Tower	7	2300	-50.1	1435.8	974.4
8__Main Tower	8	2316.667	-19.1	1587.2	910.8
9__Main Tower	9	2333.333	-3.1	1703.1	1062.2
10__Main Tower	10	2350	5.7	1693.7	1178.1
Reboiler	11	2350	17.6	525.0	1168.7

Table 4
DC-02

	Stage	**Pressure KPa**	**Temperature °C**	**Net Liquid kmol/hr**	**Net Vapour kmol/hr**
Condenser	0	1013.2	69.3	6602	0
1__Main Tower	1	1013.2	117.8	6135.1	7073.6
5__Main Tower	5	1023.9	139	6259	6748
8__Main Tower (Entry Stage)	8	1031.9	145.9	364.8	19625.3
10__Main Tower	10	1037.2	147.7	8415.7	7283.3
15__Main Tower	15	1050.6	151.3	8236.7	7200.7
20__Main Tower	20	1063.9	174.2	7584.3	6523.6
25__Main Tower	25	1077.2	182.4	7515	6386.7
30__Main Tower	30	1090.6	183.8	7519.8	6389.2
35__Main Tower	35	1103.9	184.4	7527.1	6396.3
39__Main Tower	39	1114.6	184.8	7533.5	6402.3

As stated earlier in the paper, top product from DC-01 is heated first using DC 1's bottom product (shell side) and then by water (at approximate room temperature) in order for it to reach the conditions for the reactions 1 and 2 in conversion reactor R-01, where simultaneously fresh oxygen S-10 enters. In this process, we use pure oxygen directly instead of air, because air contains about 79% nitrogen which is inert component. If it is used then this nitrogen gas will absorb most of the heat of reaction from the exothermic reaction 1. A lot of valuable heat will be lost with the nitrogen gas via the off-gas stream in such a scenario. The vapour product S-11, from R-01 enters an equilibrium reactor R-02, where reactions 3 and 4 occur, leading to the formation of methanol. The resulting stream S-13 further enters R-03, in which the same reactions take place in order to achieve higher conversion. The vapour effluents from R-03 (majorly CO2, N2) are let off directly and S-16 along with S-14 (outlet of R-02), which consist of methanol as the main component are mixed, heated and fed to another equilibrium reactor R-04, where crude DME is produced by reaction 5. S-20 comes out of R-04 and is depressurized, sent to a vapour liquid separator SEP-01 where DME gets separated from water and unreacted methanol. The isolated DME (S-22) is brought to room temperature, packed and shipped as the final product, whereas the methanol and water stream S-23, containing unseparated DME is sent to the 2nd distillation column DC-02 to separate water (S-26) from methanol and DME (S-25). S-26 (shell side) is used to heat S-22. S-25 is recycled back to R-04.

C. Operating Cost Saving

Considerations:

1. Calculations are based on the feed as described in the tables.
2. Plant is open for 330 days cumulatively in an entire year.
3. Aggregate price of electricity per unit is INR 8.76 (including energy charges, wheeling charges and regulatory asset charges) [5].

The process makes use of three heat exchangers viz. HE-01, HE-02, HE-03, HE-04. The amount and cost of electricity that would have been incurred if heaters/coolers were used instead of the proposed changes has been calculated using the heat duty data of heat exchangers from Aspen HYSYS.

HE-01:

HE-01		
Duty	3.217×10^6	KJ/h

$3.217*10^6$ KJ/h = 893.61 KJ/s

For 330 days, 22 hours each day:

893.61*330*22 KWh = 6487608.6 KWh

Cost of operating = 8.76*6487608.6 = INR 56831451.34

Similarly, for HE-02:

HE-02		
Duty	3.767×10^6	KJ/h

Cost = INR 66547822

And HE-03:

HE-03		
Duty	1.778×10^6	KJ/h

Cost = INR 31410148

HE-04:

HE-04		
Duty	7.802×10^6	KJ/h

Cost= INR 13783032

Thus, the total cost of electricity

= INR 56831451.34 + 66547822 + 31410148 + 13783032

= INR 168572453.3

In other words, INR 168572453.3 is being saved per unit feed due to the changes suggested.

3. Results

Table 5

Rxns	**Reactor**	**Equilibrium Constant**	**Conversion**	**Reaction Extent**
1 & 2	R-01	-	1. 25%	1. 323.7
			2. 75%	2. 971
3 & 4	R-02	3. 11329.29	3. 65%	3. 210.4
		4. 0.1496	4. 66.31%	4. 646.5
3 & 4	R-03	3. 11329.29	3. 99.69%	3. 112.8
		4. 0.1496	4. 0.25%	4. 0.77
5	R-04	5. 521.74	5. 79.81%	5. 482.3

4. Conclusion

ASPEN HYSYS carried out reaction 5 using the proposed method at around 175 °C and achieved almost the same conversion rate (79.81%) as that of the conventional method. INR 168572453.3 is being saved by exchanging heat of process lines instead of coolers and heaters. Thus, a sustainable method of producing DME has been mentioned in this paper.

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