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ECONOMIC ANALYSIS OF REACTIVE DISTILLATION

IN THE PRODUCTION OF TERT-AMYL METHYL ETHER (TAME)

By

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Submitted in Partial Fulfillment
of the Requirements for
Graduation with Honors from the
South Carolina Honors College

May, 2018

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Abstract

Aspen HYSYS was used to make two flowsheets, one with plug flow reactors and distillation columns and another with a reactive distillation column, to see which flowsheet was better at producing tert-amyl methyl ether (TAME) and which one was more economically feasible. The goal was to produce 15,000 metric tons of TAME per year by reacting a naptha stream with methanol. It was found that both flowsheets were capable of producing the desired amounts of TAME and with product purities around 100%. The conversions of the reactive distillation was 93.93%, significantly higher than the 72.48% and 76.98% in the base case. The cost of building the differences of the two flowsheets is shown by the bare module cost, in the base case was $719,000 and the cost of different equipment for the reactive distillation case was $364,000. The yearly cost to run the base case was $1,247,165 and $714,055 for the reactive distillation case. The reactive distillation has a cheaper initial cost which is shown by the bare module cost and has a cheaper cost to run per year. The reactive distillation flowsheet is the better flowsheet and would be the recommended flowsheet to use if this process was to be made since it has a cheaper cost to build and to operate.

Introduction

Tert-amyl methyl ether (TAME) is a chemical that is used as an additive in gasoline [5]. TAME is used to increase the octane of gasoline as well as reduce the amount of pollutants released when burning gasoline, such as carbon monoxide and some volatile organic compounds [5]. TAME is not the first chemical to be used as an additive to gasoline to increase the octane. Other oxygenates including methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and tert-amyl ether ether (TAEE) have been used, but these chemicals have issues. MTBE, a common of oxygenate, has had its usage stopped because of research suggesting that it was polluting the water supply [5]. This has caused a ban on MTBE and has led to the increase of the use of the other ethers.

Traditionally reactions and separations in chemical plants have been done separately. There will be a reactor or reactors that could vary from being a plug flow reactor (PFR), a continuous stirred-tank reactors (CSTR), or a batch reactors that will have many chemicals coming out of it that need to be separated. That stream of chemicals is then sent to a separator that could be a distillation column, an extractor, a centrifuge, or some other kind of separator to separate desirable chemicals from undesirable chemicals. There is a way to combine these two steps into one by using reactive distillation. Reactive distillation uses a distillation column to separate chemicals while also having a chemical reaction between those chemicals take place in the column. Research in reactive distillation began around the 1970s and the classic example of a successful reactive distillation column is the column run by Eastman Chemical Co. that produces methyl acetate [3]. This column was able to reduce the cost to run this process by around five times [3]. Reactive distillation can have advantages such as less equipment being needed, which lowers the capital cost of the operation, improved conversion of the reactor, improved product selectivity, and being able to overcome equilibrium limitations [2]. Not every product does benefit from using reactive distillation and in this study the use of reactive distillation in the production of TAME was evaluated [2]. Reactive distillation does not work for every system though. There are disadvantages if there are chemical with close relative volatilities, reactions that have long residence times, process conditions of reaction and distillation, for example temperature, are different, and scaling up to large flow rates [2].

TAME is commonly synthesized from reacting methanol with a naphtha mixture, which is a mixture of liquid hydrocarbons that commonly come from natural gas condensates or petroleum distillates. The chemical reaction to form TAME is the following:

$$2M1B + MeOH \leftrightarrow TAME$$

$$2M2B + MeOH \leftrightarrow TAME$$

Where 2M1B is 2-methyl-1-butene, 2M2B is 2-methyl-1-butene, and MeOH is methanol. 2M1B and 2M2B come from the naphtha mixture, but they are not the only chemicals in the mixture. The other chemicals in the mixture are isopentane, n-pentane, 1-pentene, and 2-pentene. These chemicals are not the major constituents of the mixture, but will still be in the process when the methanol and the 2M1B and 2M2B react. Since there will be other chemicals in the system, those chemicals must be separated from the product, TAME, at the end of the reaction.

Methodology

The basis for this analysis was to produce 15,000 metric tons of TAME per year using a theoretical naptha stream that was generated from a hypothetical plant and methanol that would be bought to react to make TAME. The naptha stream is made up of mostly C5s including isopentane (iC5), 1-pentene (1C5-), 2-pentene (2C5-), n-pentane (nC5), 2-methyl-1-butene (2M1B), and 2-methyl-2-butene (2M2B). Using Aspen HYSYS a process flow diagram was made for both the traditional reactor and separators, the base case, and the reactive distillation. The thermodynamic package that was used was the UNIQUAC in the liquid phase and the Peng-Robinson EOS in the vapor phase. These were chosen to help deal with the azeotropes in the system. The same feed composition and flow rate was used for both of the separation methods and the amount of equipment needed and the compositions of the product streams after the reactors and separator were recorded. The economic analysis was done in CAPCOST using the information from each flowsheet on HYSYS. The amount of equipment being used, the amount of utilities being used, and the differences in the amount of catalyst that was needed was taken into account to find out which method was more cost effective.

Results and Discussion

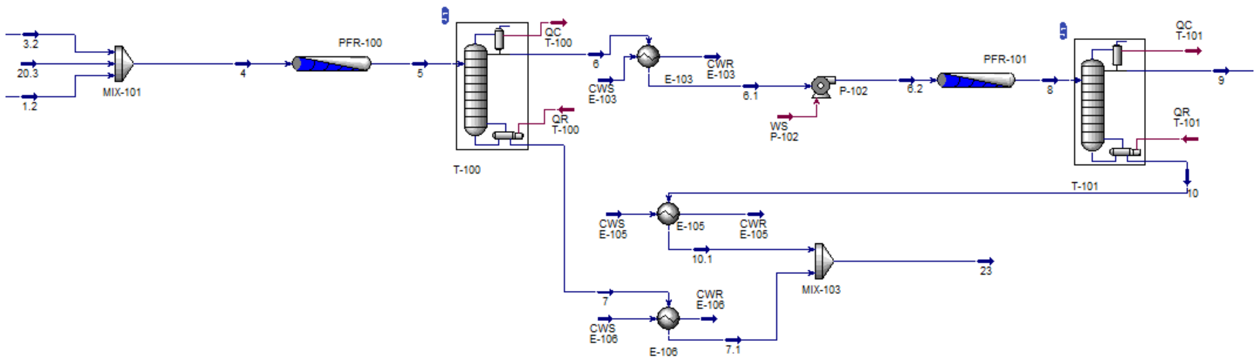

Figure 1: The process flow diagram of the base case generated in Aspen HYSYS.

Stream	1.2	3.2	20.3	4	5	6	7	6.2	8	9	10	23
Temperature (^oC)	60	60	60	60	83.91	84.28	153	60.1	67.87	82.55	153.2	40
Pressure (kPa)	548.9	548.7	545	545	521.6	500	520	620	608.4	475	525	520
Vapor Fraction	0	0	0	0	0	0	0	0	0	0	0	0
Mole Flow (kmol/h)	80	20.51	50	150.5	136.5	123.5	13	123.5	119.5	114.4	5.05	18.05
Mass Flow (kg/h)	5702	657.2	1602	7962	7962	6633	1328	6633	6633	6118	515.6	1844
Component Flowrates (kmol/h)												
H2O	0	0	0	0	0	0	0	0	0	0	0	0
iC5	38.56	0	0	38.56	38.56	38.56	0	38.56	38.56	38.56	0	0
1C5-	2.93	0	0	2.93	2.93	2.93	0	2.93	2.93	2.93	0	0
2C5-	12.44	0	0	12.44	12.44	12.44	0	12.44	12.44	12.44	0	0
2M1B	6.58	0	0	6.58	0.56	0.56	0	0.56	0.11	0.11	0	0
nC5	6.81	0	0	6.81	6.81	6.81	0	6.81	6.81	6.81	0	0
2M2B	12.68	0	0	12.68	4.74	4.74	0	4.74	1.11	1.11	0	0
Methanol	0	20.51	50	70.51	56.55	56.55	0	56.55	52.47	52.47	0	0
TAME	0	0	0	0	13.96	0.96	13	0.96	5.04	0	5.04	18.04

Table 1: The stream information for the base case.

The process flow diagram of the base case, shown in figure 1, is not the complete flowsheet of the production of TAME, it is just the reaction and separation section. Later in the flowsheet there is a methanol separation section that ends up recycling methanol and that is where stream 20.3 comes from. Stream 3.2 is the feed methanol and stream 1.2 is the feed naptha. These three streams are combined into stream 4 and then fed into the first reactor, PFR-100. As seen in table 1, this reactor produced 13.96 kmol/h of TAME, but that is not enough to produce the desired amount of TAME per year, so another reactor was need. First the product of the first reactor was put into a distillation column, T-100, and there was a good separation of TAME from the other components leaving almost pure TAME coming out of the bottoms. The tops are then sent to a heat exchanger for feed preparation to be sent into the final reactor, PFR-101. In the last reactor almost all of the 2M1B is reacted and most of the 2M2B is reacted and 5.04 kmol/h of TAME are produced. That is then sent into a distillation column, T-101, and the tops are sent to be processes later and the bottoms are combined with the bottoms of the first column to have the product stream of TAME that has 18.04 kmol/h of TAME.

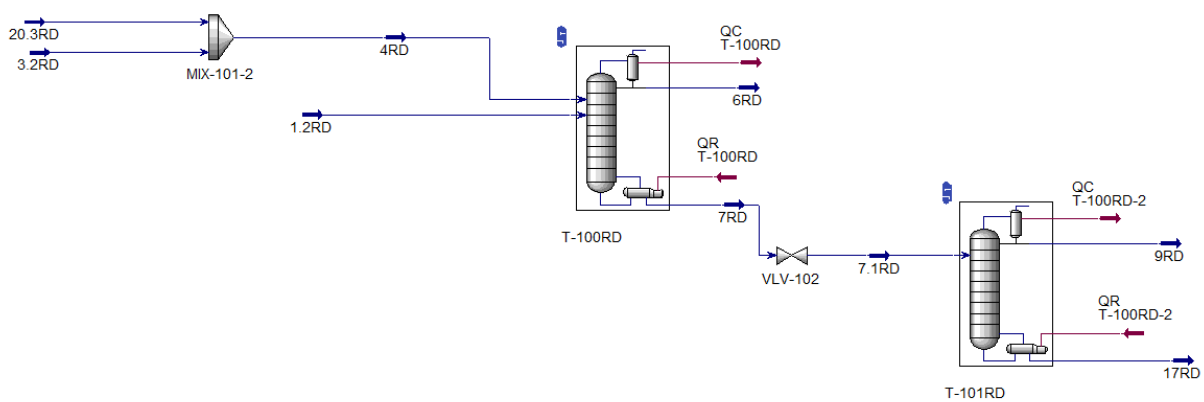

Figure 2: The process flow diagram of the reactive distillation case generated in Aspen HYSYS.

Stream	1.2RD	3.2RD	20.3RD	4RD	6RD	7RD	7.1RD	9RD	17RD
Temperature (^oC)	60	60	60	60	70.05	117.7	116.6	101.6	143.8
Pressure (kPa)	548.9	548.7	545	545	400	433	420	400	430
Vapor Fraction	0	0	0	0	0	0	0	0	0
Mole Flow (kmol/h)	80	20.51	50	150.5	93.43	39	39	21	18
Mass Flow (kg/h)	5702	657.2	1602	7962	5159	2802	2802	963.1	1839
Component Flowrates (kmol/h)									
H2O	0	0	0	0	0	0	0	0	0
iC5	38.56	0	0	38.56	38.56	0.01	0.01	0.01	0
1C5-	2.93	0	0	2.93	2.93	0	0	0	0
2C5-	12.44	0	0	12.44	5	7.43	7.43	7.43	0
2M1B	6.58	0	0	6.58	0.16	0	0	0	0
nC5	6.81	0	0	6.81	6.81	0	0	0	0
2M2B	12.68	0	0	12.68	1.01	0.01	0.01	0.01	0
Methanol	0	20.51	50	70.51	38.98	13.45	13.45	13.45	0
TAME	0	0	0	0	0	18.08	18.08	0.08	18

Table 2: The stream information for the reactive distillation case.

The process flow diagram of the reactive distillation case, shown in figure 2, is not the complete flowsheet of the production of TAME, it is just the reaction and separation section. The three feeds are the same as in the base case, in order to more easily compare the two flowsheets. The two methanol streams, 3.2RD and 20.3RD, are combined into stream 4RD and fed into the reactive distillation tower, T-100RD, and the naptha stream 1.2RD is also fed into the tower separately. The reactive distillation tower is made up of 44 trays, and has 33 trays in the reactive section with the methanol feed coming in at tray 6 and the naptha feed coming in at tray 39. As seen in table 2, this reactive distillation tower produced 18.08 kmol/h of TAME out of the bottoms and the tops had not TAME and could be process later. The bottoms did not have pure TAME though so another regular distillation column, T-101RD, was need to separate the TAME from the other constituents. From the bottoms of this tower is the product stream of TAME that has pure TAME and a flow rate of 18.00 kmol/h. The tops of the tower would be processed later in the process.

Reactor	Conversion
PFR-100	72.48%
PFR-101	76.98%
T-100RD	93.93%

Table 3: Conversion of all of the reactors on the basis of 2M1B and 2M2B.

	Base Case	Reactive Distillation
Product Purity	99.94%	100.00%

Table 4: The product purity of the two flowsheets.

The conversions are shown in table 3 and are calculated from the following equation:

$$Conversion = \frac{(2M1B\ IN + 2M2B\ IN) - (2M1B\ OUT + 2M2B\ OUT)}{(2M1B\ IN + 2M2B\ IN)} * 100$$

The two reactors in the base case had conversions of 72.48% and 76.98%, which are conversions that are relatively high, but in the reactive distillation column there was a conversion of 93.93%. This improvement of almost 20% is a significant improvement on conversion and helps save money when running a process. The reason for the increase in conversion is most likely due to how the reactive distillation column works. As the TAME is made it is separated driving the equilibrium of the reactions towards the product side causing more TAME to be made. The product purity in table 4 shows that both flowsheets were able to produce very pure TAME and that neither flowsheet had an advantage in this aspect.

Exchangers	Exchanger Type	Shell Pressure (barg)	Tube Pressure (barg)	MOC	Area (square meters)	Purchased Equipment Cost	Bare Module Cost
E-103	Floating Head	3.99	3.99	Carbon Steel / Carbon Steel	49	$ 28,700	$ 94,500

Pumps (with drives)	Pump Type	Power (kilowatts)	# Spares	MOC	Discharge Pressure (barg)	Purchased Equipment Cost	Bare Module Cost
P-102	Centrifugal	0.458	1	Carbon Steel	5.19	$ 7,010	$ 27,900

Towers	Tower Description	Height (meters)	Diameter (meters)	Tower MOC	Demister MOC	Pressure (barg)	Purchased Equipment Cost	Bare Module Cost
T-101	20 Carbon Steel Sieve Trays	12.2	1.19	Carbon Steel		4.19	$ 49,500	$ 113,000
T-102	20 Carbon Steel Sieve Trays	12.2	2.5	Carbon Steel		4.24	$ 150,000	$ 421,000

Vessels	Orientation	Length/Height (meters)	Diameter (meters)	MOC	Demister MOC	Pressure (barg)	Purchased Equipment Cost	Bare Module Cost
PFR-100	Horizontal	7	0.674	Carbon Steel		4.43	$ 7,520	$ 22,600
PFR-101	Horizontal	10	0.944	Carbon Steel		6.2	$ 12,500	$ 40,100
						Total Bare Module Cost		$ 719,100

Figure 3: The capital cost of the base case generated in CAPCOST.

Towers	Tower Description	Height (meters)	Diameter (meters)	Tower MOC	Demister MOC	Pressure (barg)	Purchased Equipment Cost	Bare Module Cost
T-101	44 Carbon Steel Sieve Trays and 46.4 meters of Plastic Saddle	23.2	1.08	Carbon Steel		4.33	$ 93,500	$ 215,000
T-102	30 Carbon Steel Sieve Trays	18.3	1.15	Carbon Steel		4.3	$ 68,300	$ 149,000
						Total Bare Module Cost		$ 364,000

Figure 4: The capital cost of the reactive distillation case generated in CAPCOST.

The capital cost for the base case is shown in figure 3 and for the reactive distillation case in figure 4. These figures were generated in CAPCOST with a CEPCI value of 567.5, the value for the year 2017, to adjust for inflation. In the base case there are six pieces of equipment that were taken into account, a heat exchanger, a pump, two distillation columns, and two reactors. From the specifications of those equipment that was found from HYSYS the cost associated to build all of those pieces of equipment is $719,100. The reactive distillation case only had two pieces of equipment, the reactive distillation tower and the regular distillation tower. From the specifications of those equipment that was found from HYSYS the cost associated to build all of those pieces of equipment is $364,000. When just looking at the cost to build the plant it costs more money to build the base case than the reactive distillation case.

Name	Total Module Cost	Grass Roots Cost	Utility Used	Efficiency	Actual Usage	Annual Utility Cost
E-101	$ 111,000	$ 159,000	**Cooling Water**		172000 MJ/h	$ 510,000
P-101	$ 32,900	$ 44,300	Electricity	0.7	0.654 kilowatts	$ 329
T-101	$ 134,000	$ 189,000	NA			
T-102	$ 496,000	$ 666,000	NA			
V-101	$ 26,700	$ 38,000	NA			
V-102	$ 47,300	$ 66,100	NA			
Totals	**$ 848,000**	**$ 1,160,000**				**$ 510,000**

Figure 5: The cost of utilities for the base case generated from CAPCOST.

Name	Total Module Cost	Grass Roots Cost	Utility Used	Efficiency	Actual Usage	Annual Utility Cost
T-101	$ 254,000	$ 353,000	NA			
T-102	$ 176,000	$ 249,000	NA			
Totals	**$ 430,000**	**$ 602,000**				**$ -**

Figure 6: The cost of utilities for the reactive distillation case generated from CAPCOST.

Utility	Cost ($/GJ)
Electricity	16.8
Cooling Water	0.354

Table 5: Table of the prices per energy for the utilities needed.

The cost of utilities for the base case is shown in figure 5 and for the reactive distillation case in figure 6. In the base case there are six pieces of equipment that were taken into account and only two of them had utilities costs associated with them, the heat exchanger and the pump. Using the costs from table 5, the annual utilities cost for the base case was found to be $510,000. The reactive distillation case only had two pieces of equipment, the reactive distillation tower and the regular distillation tower and neither of those had utilities costs associated with them meaning the cost of utilities for the different pieces of equipment in the reactive distillation flowsheet had no cost with them.

Base Case	
Volume of PFR-100 (m^3)	2.5
Bulk Density of PFR-100 (kg/m^3)	1575
Weight of Catalyst in PFR-100 (kg)	3937.5
Volume of PFR-101 (m^3)	7
Bulk Density of PFR-101 (kg/m^3)	1575
Weight of Catalyst in PFR-101 (kg)	11025
Total Weight of Catalyst	14962.5
Cost of Catalyst per year	$49465

Table 6: The cost of the catalyst in the base case.

Reactive Distillation	
Volume of T-100RD (m^3)	15.23
Bulk Density of T-100RD (kg/m^3)	1575
Weight of Catalyst in T-100RD (kg)	23973.2
Cost of Catalyst per year	$79255

Table 7: The cost of the catalyst in the reactive distillation case.

Since the feeds for the two flowsheets is the same the cost of the raw materials for the two flowsheets is the same expect for the cost of the catalyst. The catalyst is amberlyst 15 and needs to be replaced three times a year with a cost of $1.16/kg. The amount of catalyst needed was dependent on the volume of the reactors in the base case and the volume of the reactive section in the reactive distillation case. The volume and densities of the reactors in the base case can be seen in table 6. The cost per year of the catalyst in the base case is $49,465 per year. The volume and the density of the reactive section of the reactive distillation column are shown in table 7. The cost per year of the catalyst in the reactive distillation case is $79,255. More catalyst is needed in the reactive distillation case although the cost is not difference between the two is not that significant.

	Base Case	Reactive Distillation
Towers for N_{np}	2	2
Reactors for N_{np}	2	0
Heat Exchangers for N_{np}	1	0
Total for N_{np}	5	2
Cost of Labor per year	$687700	$634800

Table 8: Cost of labor for both flowsheets.

The cost of labor was determined by this equation:

$$Cost\ of\ Labor = \frac{\$52900}{year} * 4.5 * (6.29 + 31.7 * P^2 + 0.23 * N_{np})$$

In the equation P is the processing steps that include handling of particulate solids, which for both of the cases is zero. The salary of each operator needed is $52,900 per year and the N_{np} is determined based off of the number of certain types of equipment. The equipment included in the calculation for N_{np} is shown in table 8. After the calculation was performed it was determined that one more operator was needed for the base case and the cost of labor for the base case was $687,700 per year and was $634,800 for the reactive distillation case.

	Base Case	Reactive Distillation
Bare Module Cost	$ 719,100.00	$ 364,000.00
Cost of Utilities per year	$ 510,000.00	$ -
Catalyst Cost per year	$ 49,465.00	$ 79,255.00
Cost of Labor per year	$ 687,700.00	$ 634,800.00
Total Cost per year	$ 1,247,165.00	$ 714,055.00

Table 9: Summary of all of the costs associated with each flowsheet.

In table 9 there is a summary of all the costs associated with each of the flowsheets. The initial cost is shown in the first row, the base case is more expensive than the reactive distillation case in the initial cost to build the equipment. Then looking at the cost per year the base case costs $1,247,165 per year and the reactive distillation case costs $714,055 per year. The base case also cost more to operate per year than the reactive distillation case.

Conclusion

When comparing the base case to the reactive distillation case the first part to compare the differences between the two flowsheets. With the same feeds both flowsheets were able to produce around the same amount of TAME with the base case producing 18.04 kmol/h and the reactive distillation column producing 18.00 kmol/h. The base case had a product purity of 99.94% and the reactive distillation column had a product purity of 100.00%, so both flowsheets had around the same product purity. The difference was the base case reactors had conversions of 72.48% and 76.98% while the reactive distillation column had a conversion of 93.93%. The reactive distillation column caused there to be a higher conversion most likely due to it being able to help push the equilibrium towards the product side by removing the product soon after it forms. When comparing the economic aspect of the two flowsheets there were significant differences. The different equipment for the base case included two distillation columns, two reactors, one heat exchanger, and one pump that had a bare module cost of $719,000 and the different equipment for the reactive distillation included only two distillation columns and had a bare module cost of $364,000. The yearly cost for the base case was $510,000 for utilities, $49,465 for the catalyst, and $687,700 for labor which has a total of $1,247,165. The yearly cost for the reactive distillation was $0 for utilities, $79,255 for the catalyst, and $634,800 for labor which has a total of $714,055. The reactive distillation has a cheaper initial cost which is shown by the bare module cost and has a cheaper cost to run per year. The reactive distillation flowsheet is the better flowsheet and would be the recommended flowsheet to use if this process was to be made since it has a cheaper cost to build and to operate.

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