

CHEMICAL ENGINEERING BACHELORS RESEARCH PROJECT

Title: Determination of the techno-economic viability for the conversion of glycerol to BTX

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Research problem: Glycerol has been identified as an attractive sources for the synthesis of benzene, toluene and xylene by a process known as catalytic pyrolysis. Within the NWO-LIFT project, Songbo and co-workers have investigated this process in detail and interesting leads have been discovered to optimize BTX yields. In this bachelor research project, we will determine the techno-economic viability of the conversion of glycerol to BTX based on a design made in Aspen.

Keywords: green chemicals, bio based economy, waste stream valorization,

Contact person from industry (if applicable and including name, email, name of company):

BIOBTX

Abstract:

The techno-economic feasibility of a catalytic glycerol pyrolysis plant was investigated using ASPEN PLUS software. A total yield for benzene, toluene and xylene (BTX) on glycerol was reached at 25.4% at a total capacity of 300kt/yr.

The process was thought to be techno-economically feasible under the specific design in the paper. The equipment and installation cost of the process was not a main determinant of the economic feasibility but rather the operating cost including raw materials and catalyst. At the current average market price BTX of approximately 480 euros/ton, a catalyst cost at 1300 euros/ton and an energy consumption of 190 million KWh. The design has an annual profit of 4 million and a payback time of 16 months.

a conversion of 25.4% was reached and is courage to have further investigation towards increasing the total conversion of BTX to have a more promising profitability by having a more stable response towards the price fluctuation of raw materials.

Introduction:

As the effects of global climate change becoming more noticeable the demand for a more sustainable utilization of chemicals increased significantly. Mainly to reduce and eventually replace the heavy usage of fossil fuel, therefore, a replacement needs to be found. Various different approaches for reaching this goal has taken place and the growth of bio-diesel industry is one in many noticeable evidences for such a development. As a result, the production of crude glycerol as a primary co-product of bio-diesel industry also increased and is predicted to reach a total global production of 6 million tons in 2025 [1,2].

As glycerol is often regarded as an important sustainable source for various industrial usage because it is more stable than solar and wind power [3]. Although it has a relatively low energy density, it could be converted into more energy dense products such as liquid fuels, one interesting route is to pyrolyse glycerol through porous zeolite catalyst to form light aromatics such as benzene, toluene and xylene, namely bio based BTX. These bio based BTX could be used as fuel additives or as various starting and/or intermediate chemical for numerous industrial synthesis. In this way, the catalytic pyrolysis of glycerol could be favored as multi-purpose.

There are various types of catalysts used to perform this pyrolysis process and have shown promising results. During this investigation, data from a heterogeneous zeolite catalyst, H-ZSM-5/bentonite (60/40), was used to simulate the catalytic pyrolysis of glycerol. During the pyrolysis process, the glycerol was first vaporized, the vaporized glycerol was then dehydrated, mostly into oxygenates such as acrolein and acetaldehyde; these oxygenates then underwent acid-catalyzed aldol condensation and cyclization etc. to form aromatics [4].

The pyrolysis process gives three major type of products. Liquid products are formed through a free-radical mechanism and a series of reactions such as dehydration, decarboxylation, tautomerization and decarbonylation [5,6]. The gaseous products are formed through thermal decomposition of pyrolysis products [7-9]. And the coke is formed mainly through the polymerization of the intermediates of pyrolysis product and their decomposition products [10,11].

During the process, catalyst deactivation is observed and the deactivated catalyst was regenerated through oxidation at 600 °C to remove the coke deposited on the catalyst. However, after regeneration of catalyst, an irreversible deactivation occurred causing a decrease in activity of regenerated catalyst. The regenerated catalyst was tested to have an activity 91.5% to that of the fresh catalyst [4].

The product of such pyrolysis process often separates into aqueous and organic phases where light aromatics are present in organic phase along with other organic soluble products such as heavy aromatics, light paraffin and olefin. The yield for BTX on crude glycerol feed on a batch gram scale unit was 15.5 wt% and a yield of 8.1 wt% was reached for crude glycerol on a continuous bench scale unit. The difference in weight yield for BTX was thought to be a result of different heating rates for glycerol and a slightly different operating temperature between the two experiments. It was rationalized that a lower heating rate often results in an increase in the production of coke on catalyst causing catalyst deactivation and thus a decrease in BTX yield [4].

It was then discovered that recycling of heavy aromatics in the products could result in an increase in BTX yield. The heavy aromatics in this case were polycyclic aliphatic (PCA) and polycyclic aromatic hydrocarbons (PAH). Both of these two compounds were co-fed with glycerol on a 1-1 weight feed ratio. The combination of PAH and crude glycerol on a continuous bench scale unit resulted in a 15 wt% yield on feed for BTX and the combination of PCA and crude glycerol on a continuous bench scale unit resulted in a BTX yield of 16 wt% on feed. In addition to this, it was also discovered that the formation of more smaller alkanes and alkenes upon the ease of aliphatic ring-opening, these smaller alkanes/alkenes are considered to be the precursors for aromatics and is considered to have a positive effect on the BTX yield [12]. Therefore, with a BTX yield over 15 wt% on feed, the realization of such a plant is becoming specific with effective recycling streams of light alkanes/alkenes (C₁-C₃) and heavy aromatics. Bio-based BTX production was then thought to be possible in real life.

Considering its possible benefits, the economic feasibility of such a process became a target of interest. Therefore, this thesis explores a small production plant of bio based BTX at an annual production quantity of 100 kiloton (combined mass of benzene, toluene and xylene) from an input of 1272 kiloton of crude glycerol.

The plant consists of a moving bed reactor, regeneration oven for the deactivated and coke-rich catalyst, separation of products and recycling of heavy aromatics and light olefin and paraffin (mostly C₁-C₃).

The aim of this thesis is to answer two questions and its sub questions.

1. Is such a plant profitable?
 - a) What effects the profitability?
 - b) If such a plant is not profitable, what could be done to improve its profitability?
2. What is the final theoretical conversion for BTX after recycling.

It is hypothesized that the process ought to be profitable at a lower production scale and depending on the price for BTX individually and as a mixture, the profitability of this plant could be rather flexible. The final theoretical yield for BTX on glycerol after recycling should be at around 25%.

Experimental:

Assumptions:

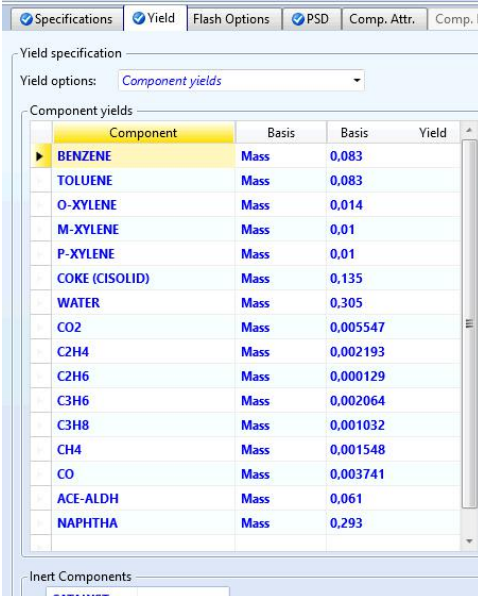
Reactor model was based on the yield of the reaction through experimental data, specific reaction kinetics was not modeled. It was also assumed that a feed of crude glycerol to heavy aromatics weight ratio of 2:1 has similar effects as a weight ratio of 1:1. In addition to that, the recycling of light alkenes/alkanes was assumed to have a 4% increase in BTX yield on feed, reaching an overall 20 wt% yield on feed. Furthermore, during the deactivation process of the catalyst, the activation of the catalyst would decrease with the increase of regeneration times; the catalyst was assumed to reach a constant activity of 90% to that of the fresh catalyst after 10 times regeneration. As

a result of permanent catalyst deactivation, a part of catalyst must be discarded and new catalyst feed must compensate for that loss.

It was also assumed that the heat generated from the regeneration furnace is sufficient to supply the heat needed to keep the pyrolysis reactor at the desired temperature. This is assumed because of the heat generated from the furnace is far larger than that of the heat needed for the pyrolysis reactor.

Modeling of the process:

The catalytic pyrolysis of glycerol takes place in a moving bed reactor to convenient the catalyst replacement process. The reactor is modeled using RYield and is set to operate at 1 bar and at 550°C. The specifications of the reactor are shown in figure 1. The final yield for BTX is assumed to be 16 wt% with heavy aromatics recycle using the data from *H.C.Genuino et al [12]* and 20 wt% with light alkanes/alkenes recycle. Naphthalene was used to represent the heavy aromatics and acetal-aldehyde was used to represent other organic products. Furthermore, the yield ratios of each component is assumed to correspond to the data from *S. He et al [4]*. Coke was represented using graphite and is assumed to not participate in reactions and stays as solid throughout the reaction, the same principle applies to catalyst, which is modeled using alumina and is assumed to remain as solid throughout the reaction.



Component	Basis	Yield
BENZENE	Mass	0,083
TOLUENE	Mass	0,083
O-XYLENE	Mass	0,014
M-XYLENE	Mass	0,01
P-XYLENE	Mass	0,01
COKE (CISOLID)	Mass	0,135
WATER	Mass	0,305
CO2	Mass	0,005547
C2H4	Mass	0,002193
C2H6	Mass	0,000129
C3H6	Mass	0,002064
C3H8	Mass	0,001032
CH4	Mass	0,001548
CO	Mass	0,003741
ACE-ALDH	Mass	0,061
NAPHTHA	Mass	0,293

Figure 1

The feed stream consists of crude glycerol and recycle streams. The composition of crude glycerol was modeled using data from *S.He et al [4]* and the recycle streams constitutes of mainly naphthalene and light alkenes/alkanes.

Catalyst was also recycled after the removal of coke using furnace. A part of the catalyst was discarded as a result of irreversible catalyst deactivation and this amount is the same amount of the feed catalyst. The furnace was designed to keep the temperature at 600°C at 1 bar to ensure effective removal of coke on the catalyst. The specific modeling of the combustion process was calculated using built-in algorithm from ASPEN PLUS to generate combustion reactions with Nitrogen monoxide, NO as NO_x product.

After the pyrolysis reactor, all products are in gas phase and was brought to the separation and purification process. This process for BTX was completed in two steps. The first step is to separate the two insoluble phases: organic and aqueous. This step is achieved using two flash columns and two decanters. The gaseous products were first cooled down to 75°C and was brought to a flash column to separate liquid phase from gaseous phase. The liquid phase was the directed to a decanter to remove naphthalene from water. The separated naphthalene was then recycled to the pyrolysis reactor with a purge line and water was discarded. The gaseous product after the first flash column was directed to another cooler where the vapors were further cooled to 20°C to condense rest of the liquid. This vapor-liquid mixture was then again directed to a flash column and the two phases were then separated. The gaseous phase was recycled to the pyrolysis reactor with a purge line. The liquid phase was directed to another decanter to further remove the water from the products. After the second decanter, all the product was directed to the first distillation column. There are four

distillation columns in total, the first column was designed to remove any dissolved gases and the last three were to separate benzene, toluene and xylene into individual products of >95% purity.

A complete diagram of the model is shown in figure 3 and a cost estimate was then brought out using the designed model.

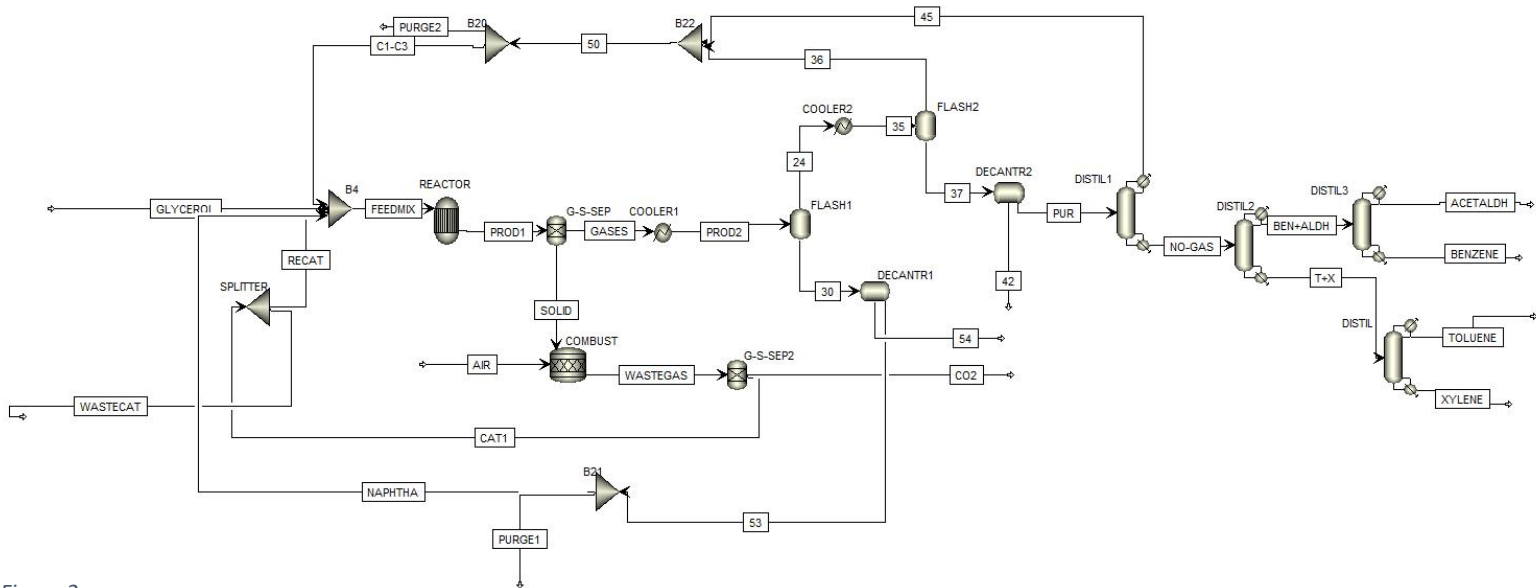


Figure 2

Results:

The cost estimate performed consists of two different aspects. The first one being the equipment and installation cost, the second one being the utility cost. The equipment cost for each individual part of the process was calculated using the data provided in the ASPEN PLUS simulation such as vapor flow rate, volumetric flow rate and energy consumption etc. and from the book *Towler and Sinnott, 2013 [13]*. The annual cost and revenue for the process are listed in table 1. The cost of

Name of Equipment	Purchase equipment cost (\$)
Pyrolysis Reactor	586572
Combustoin Reactor	110078
Cooling tower	126406
Flash column 1	40587
Flash column 2	14730
L-L Separator 1	266069
L-L Separator 2	279546
Distillation column 1	37891
Distillation column 2	64361
Distillation column 3	52952
Distillation column 4	68661
Total equipemnt cost per equipment (\$)	
Name of Equipment	Purchase equipment cost (\$)
Pyrolysis Reactor	1877030.4
Combustoin Reactor	352249.6
Cooling tower	404499.2
Flash column 1	129878.4
Flash column 2	47136
L-L Separator 1	851420.8
L-L Separator 2	894547.2
Distillation column 1	121251.2
Distillation column 2	205955.2
Distillation column 3	169446.4
Distillation column 4	219715.2

Figure 3

the moving-bed reactor was estimated using a fixed bed reactor with catalyst since a moving-bed reactor is essentially a fixed-bed reactor that accommodates slow movement of the solids [13] and in this case the recycling of catalyst. Cost estimation for the fixed bed reactor with catalyst and the two decanters were done using *Woods, 2007[14]*. It could be seen from the table that the annual revenue is dependent on the product price and total annual cost is dependent on the glycerol and catalyst price. It could be seen from the table that the cost of the equipment is rather low when compared to the annual revenue. It is the prices for the crude glycerol, catalyst and product price.

The cost for the equipment can be found in figure 3 and it could be seen that the equipment cost is not very high when compare to the production sales.

The operating cost, including raw material, catalyst and energy supply could be calculated. The price for crude glycerol was set to be 50

euro/ton in a range of 50-200 \$/ton at a feed rate of 1183kt/yr. The price for the catalyst was set to be at 1300 euro/ton at a feed rate of 89kt/yr. And the energy cost was calculated using burning of gasoline at a cost of 0.0024ct/kwh.

The final annual profit was estimated to be at over 4 million euros. Thus the payback time for such a plant is less than 2 years.

The specific calculations regarding the equipment cost is in figure 3 and calculations regarding the operating cost is in figure

Raw materials	Cost (euro/year)
Glycerol (50/t)	59150000
Catalyst (1300/t)	115700000
Utility cost per year (euro)	
190319760 kwh with 0.026ct/kwh at 75% burning efficiency	6597751.68
Product sells:	
Benzene (450 euro/t)	76050000
Toluene (446 euro/t)	77158000
Xylene (460 euro/t)	32374800
Annual revenue	185582800
total anual cost(euro):	181447751.7
4 Total Annual Porfit(\$):	4135048.32

Figure 4

Discussion:

The model for catalytic pyrolysis of crude glycerol over zeolite was estimated to have a 20 wt% BTX yield on feed and a final yield of 25.4 wt% on crude glycerol.

A continuous unit without the recycle streams usually have a BTX yield of 8-9 wt% on feed [4,12], the recycling of heavy aromatics increased such a value to 16 wt% and the recycling of gaseous products, mainly light alkenes/alkanes, was estimated to increase the weight yield to 20 wt% on feed.

The equipment cost is rather little when compared to the annual operating cost including raw materials. Therefore, a insufficient total BTX weight yield was thought to be the main determinant for such a plant to be profitable. In order to rationalize results and to suggest future investigations, the assumptions were again examined.

The first assumption made in the model is that a feed of crude glycerol to heavy aromatics weight ratio of 2:1 has similar effects as a weight ratio of 1:1. 16 wt% yield for BTX was an experimental value and the reason for it to increase the BTX yield was that heavy aromatics increases the BTX weight yield by supplying it with additional reactive intermediates to the aromatization to BTX. Heavy aromatics breaks into smaller fragments and these fragments are intermediates for the aromatization to BTX. Therefore, having less heavy aromatics in the feed could mean a decrease in the additional supplies of reactive intermediates which could ultimately decrease the BTX yield. However, this is to assume that the relation between the amount of heavy aromatics co-feed and BTX yield is linear, there might also be an optimal heavy aromatics co-feed amount for the given reaction

condition. This could require further investigation using the same amount as the heavy aromatics in the product.

Another assumption made in the model is that the recycling of light alkenes/alkanes would result in a 4% increase in the weight yield for BTX on feed while the recycled light alkenes/alkanes only occupies 1.63 wt% in the feed. This assumption was made because of a high hydrogen/carbon ratio of these light alkenes/alkanes. To form a mole of BTX from these light alkenes/alkanes, excess hydrogen atoms must be released due to its high hydrogen to carbon ratio. The presence of hydrogen is considered to be beneficial for the aromatization of BTX [4] and thus having a greater increase in BTX than the actual weight percentage of recycled gases. This essentially suggests that the recycled gases could not only form BTX by itself, it could also affect the pyrolysis environment by supplying it with extra hydrogen. The effect of such hydrogen rich compounds could be further investigated by adding hydrogen rich light alkenes/alkanes present in the product individually, though the effect of individual co-feed gas on the pyrolysis could be different when other gases are present. Therefore, this requires further investigation.

On the other hand, the catalyst deactivation during the process was assumed to have a constant 10 wt% permanent deactivation after 10 times regeneration. This needs to be investigated as the catalyst deactivation is also an important factor affecting the annual cost of the process. If the catalyst has a maximum deactivation weight percentage as assumed, the cost of such process would decrease.

Besides the assumptions, a significant water content was also worth noticing. It was investigated that a water-diluted glycerol feed has a BTX yield of 16.5wt% [4]. This yield is significantly larger than having only crude glycerol as a feed and the effect of water on the pyrolysis of this process could be investigated, the optimal ratio of water and crude glycerol could be determined.

Lastly, due to the current outbreak of CoVid-19, the demand for oil market decreased significantly causing a decrease in the crude oil price and thus a decrease in the BTX market price [15]. This also shows a very versatile price margin for different occasions. For example, if the government imposes a tax on gasoline product to encourage sustainable development pathway, causing an increase in the price of BTX, this process would be easier to be profitable. Or if the crude glycerol production is such that it has a large surplus causing a very low even negative purchase price, this process would also benefit greatly.

It is also possible that the price for catalyst and crude glycerol increase to an extent where it is no longer profitable. For example, at current product price point (on average 480 euro/ton) and catalyst price point (1300 euro/ton), if the price for crude glycerol increases to 60 euro/ton, then the process is no longer profitable with a deficit of 7.6 million per year. This depicts the other side of the story, if the prices for raw material increases, the process soon becomes non-profitable due to a BTX yield of 25.4 wt% on crude glycerol.

Conclusion:

In conclusion, with the current design of overall 25.4 wt% BTX yield, it is possible, both technically and economically, to have a bio-based BTX production process through catalytic pyrolysis of crude glycerol. The main determinants for the economic feasibility for such a process are the BTX yield, raw materials cost and product market price. Thus it was attempted to recycle gaseous products and heavy aromatics to increase the overall yield for BTX based on current assumption. Numerous research could be done in order to obtain a clearer vision of the effects of water, light alkenes/alkanes and heavy aromatics in terms of their optimal co-feed quantity to achieve a self-sustaining process with minimal input. With a lower raw material cost and higher product market price, the significance of the BTX yield is decreased. However, in order to ensure the process is economically feasible in most price margins, it is thought to be better to have a higher BTX yield on crude glycerol.

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Appendices:

A. Detailed depiction of the APEN PLUS model:

