Distillation of Effluent Polystyrene Pyrolysis Stream

A Major Qualifying Project
submitted to the Faculty of
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
degree of Bachelor of Science
in
Chemical Engineering

By

Connor Mulvey

Parshon Sorornejad

Date:
May 6th, 2021
Report Submitted to:

Michael Timko
Worcester Polytechnic Institute

Abstract

This project focuses specifically on the separation aspect of the distillation of an effluent pyrolysis stream. Separation is important to understanding how to deal with polystyrene waste and sustainably create more polystyrene in the future. The separation of the polystyrene was simulated in ASPEN Plus. The results of the ASPEN simulations show that these optimal values are reached around a reflux ratio of 0.4 and a feed composition of 85% monomer. The column produces styrene monomer at a composition of around 93% with the optimal operating cost. The distillation column set up in the idealized operating conditions allows for the most reasonable production of it at that purity. Operating costs are an important factor in the process of polystyrene pyrolysis and distillation, because the end product, styrene monomer, should be competitive in price with of freshly produced styrene to help reduce total necessary plastic production.

Acknowledgments

We thank professor Timko for helping us through our MQP and for his ever-present availability and guidance on our project. We are also thankful to the thank WPI Chemical Engineering Department for providing us with the opportunity to complete our MQP.

Table of contents

List of Figures

List of Tables

Introduction

Polystyrene is used in a variety of products due to its many potential applications. Styrene is often used to manufacture products like plastic bottles and many containers. The versatility and ability to cheaply produce styrene products has allowed for a lot of consumption, but the waste that these products have produced has not been sustainably dealt with. Plastic waste is one of the largest problems facing the environment, and that is because it has not been dealt with as a problem due to its often-marketed reusability. Plastics are generally single use and therefore are not great alternatives for re-use in many products, creating accumulation. For plastics like polystyrene to have a continued use, more sustainable practices to create these polymers must be created and implemented to prevent long terms risks to the global ecosystem.

The scale is also increasing as the 42.7-billion-dollar industry increases exponentially each year (Cision, 2020; Intrado, 2020). Last year, 15.61 metric tons of polystyrene were produced worldwide and should continue to grow (• PTA Production Capacity Globally 2023 | Statista, 2021). Plastic demands increased with the growing middle class, which has started to grow more rapidly across Asia as they have industrialized. Plastic consumption grows with the middle class as most of the consumption of plastic centers around many common products like meat and poultry, which increases as wealth rises (Cision, 2020; Intrado, 2020). Plastics are almost never biodegradable, and there are increasingly limited areas for places to dispose of waste (Park et al., 2003).

The majority of plastics currently end up in landfills, as little over 75 percent plastics in the United States are in landfills and only 8 percent of plastic is actually being recycled. Plastic in landfills can take hundreds of years to decompose, and sometimes the act of being in a landfill can increase this time since it reduces when in exposure to outside elements. Worse than landfills, plastics can often end up in the environment, with large portions accumulating in the ocean. An increasingly larger portion of plastic waste has also started to be burned for energy over the past few years in the United States, which decreases the need for landfill space. This practice is often more common in Europe, but it is starting to be adopted in the United states due to the lack of any other sustainable methods. Plastic incineration at least reduces the potential plastic pollution, but the process does have adverse greenhouse gas effects which can be slightly offset by different catalytic converters and absorbers (EPA, n.d.). The common form of recycling involves melting down the plastic and re-processing it, which usually reduces the quality and malleability of the plastic. Additionally, the quality requirements for feed streams are often rather high since many recycled materials contain food contaminates or other impurities that disqualify a lot of plastic waste from being recycled.

Re-use is better than incineration, landfills, and re-melting (Liu et al., 2000). Another method to recycling plastics is through pyrolysis. Pyrolysis is performed by heating the plastics enough to break the chains of the polymer, reducing them into plastic monomers and other products. The pyrolysis of polystyrene is a complex process that involves the heat breaking down the larger polymers. Yields of the different components vary based on many factors, such as the

operating conditions like temperature and pressure as well as the reactor being either catalytic or some sort of reactor like a fluidized bed (Aguado et al., 2003).

New plastics can be created out of these monomers in exactly the same way that the original plastics were created. Polymerization for polystyrene often requires high purity of monomers, which once held at higher temperatures, can come together to create different types of polystyrene plastics based on the polymerization conditions. The outcoming effluent streams of pyrolysis reactions for polystyrene are often majority styrene monomer but are not nearly close enough for an industrial-setting polymerization stream. The styrene monomer can be separated from the other parts of the pyrolysis stream by utilizing its physical properties that differed from the other pyrolysis components.

The pyrolysis stream is usually composed of a variety of different molecules which can be roughly grouped by their weights into heavies and lights. Based on the vapor pressure of these different streams, the heavies and the lights can be separated through separators like a distillation column. Lighter molecules will generally have higher vapor pressures at temperatures allowing them to travel off as vapors. These can be condensed in a product stream, which then could potentially be used to repolymerize polystyrene. In this process there will be a waste stream, so not all of the styrene will be recovered, but fine tuning the process can yield higher results.
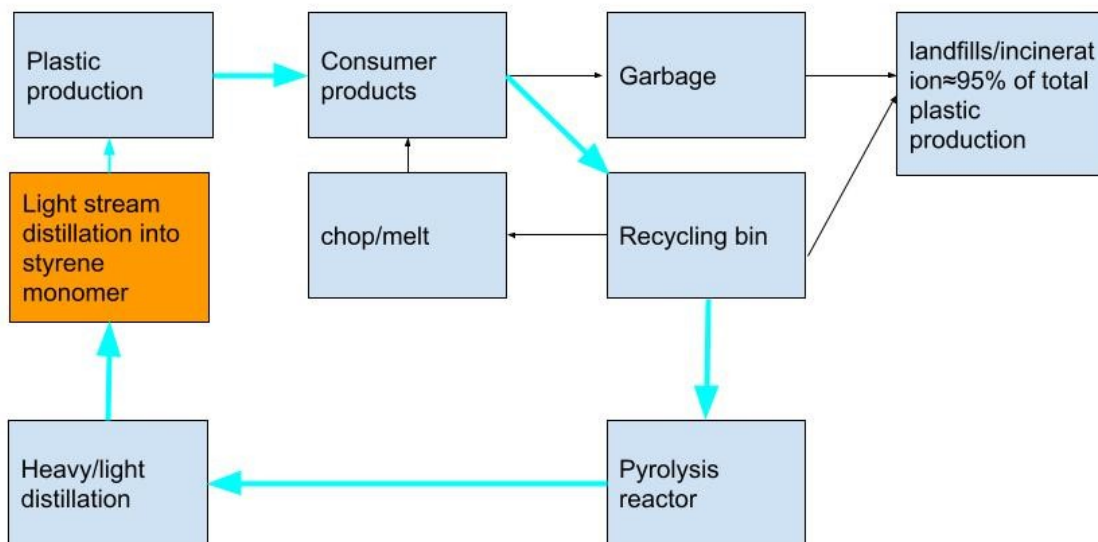
Figure 1. Process outline Diagram

This project focuses specifically on the separation aspect, as shown in the orange box in Figure 1. Separation is important to understanding how to deal with polystyrene waste and sustainably create more polystyrene in the future. One of the main things currently hindering recycling and more sustainable ways to degrade plastics is the current economics of the production of plastics in the often-infeasible processes of recycling methods. Although it is probably not possible to overcome the financial viability of creating new styrene monomers as opposed to once separated from a pyrolysis reaction, if the difference is lessened potentially with government regulation or subsidies, it will become a more viable method in the future.

Background

This section provides an overview on Pyrolysis reaction, different pyrolysis reactors, vapor pressure models, and distillation.

Pyrolysis reaction

Pyrolysis reactions are fairly complex and can have several different products that can be generally categorized as gaseous, liquid or coke (Aguado et al., 2003). Pyrolysis reactions generally occur around 300 to 900 degrees Celsius and involve the degradation of the carbon-carbon bonds in organic compounds. Pyrolysis at higher temperatures is known as fast pyrolysis because the reaction speeds are greater for the degradation of the bonds. Slow pyrolysis occurs around the lower end of the range at about 300 degrees Celsius. The higher temperature overall affects the average weight of the product streams, thus slow pyrolysis produces more solid organics while fast pyrolysis produces liquid organics (Student Energy, n.d.). The process is anaerobic because oxygen would create combustion at high temperatures forming carbon dioxide in water from the polystyrene. Usually, these reactions are run in the presence of inert gases to prevent any combustion, allowing for the chains to be broken down and not attach to any foreign elements. The solid plastic that is made up of long chain polymers mostly becomes a liquid as chain length is reduced, increasing the melting temperature. A small portion becomes gas which is composed of compounds like propane, ethane and some hydrogen that's created in the dehydrogenation processes. The coke is a tar formed in the part of the process where flow can be slow over intensive heat sections, causing the liquid stream to harden (Hassan et al., 2016; Liu et al., 2000).

During the pyrolysis reaction, the following types of reactions are taking place: chain fission, radical recombination, carbon–hydrogen bond fission, hydrogen abstraction, mild-chain β-scission, radical addition, end-chain β-scission, 1,5-hydrogen transfer and disproportionation (Aguado et al., 2003; Kruse et al., 2001). When the polystyrene is first heated up, the energy can cause some of the covalently bonded carbon to undergo homolytic fission, resulting in two radicals. These first two reactions that occur are called initial fissions, resulting in chains of polystyrene with a radical at the end. Some of these chains undergo radical recombination and join together in an equilibrium relationship with the chain fission. The hydrogen-carbon bonds are also undergoing fission and attaching to other radicals on the carbon of other chains in hydrogen abstraction. As the chains start to get smaller, mid-chain fission and radical addition occur as chains with a radical split creating a double bond on one and a radical on the other. The double bond can then split again, creating the styrene monomer in end-chain β-scission, which is the most common result in this reaction (Kruse et al., 2001).

Some of the resultant chains end up as trimers and dimers, which do not all undergo additional fissions. As the average amount of energy or heat of the reactor increases, these bonds would eventually break. A greater fraction of the molecules would also completely dehydrogenate under the large amount of energy and form pure carbon chains. These carbon chains are solids that would build up in the process. The right energy levels to balance the larger portions of styrene monomer being formed and preventing the styrene from completely dehydrogenating involve

3

specific environments and catalysis to direct the reaction towards the ideal outcome (Kruse et al., 2001).

Estimating the results for pyrolysis reactions are rather difficult to computate since the initial products do not have uniform feeds. Most calculations take an average of all the properties, like the average moment to calculate the potential reactions. Estimates can be useful for designing reactors because often all experimental data can observe is the end results of the pyrolysis streams, so understanding the mechanism can help improve desired yields (Kruse et al., 2001, 2002).

Pyrolysis reactors and effluent stream compositions

Plastics have a relatively irregular material making pyrolysis reactors more difficult to design. Most reactors will intake a feed of plastics that have been cut up into pellet form. This makes it easier to feed into the vessel as a stream, and it increases the surface area of the material (Park et al., 2003). Plastics are generally low density and have variable textures, so reactors need to account and make use of these properties to have favorable operating conditions.

The products of a semi-batch reactor in Korea found yields of different compositions based on temperature, catalysts and time. In this reactor, the styrene composition was affected by different factors like whether more a-methyl styrene was present. The components they were mainly looking at in the pyrolysis effluent streams were benzene, toluene, ethylbenzene, a-methyl styrene, styrene and the styrene dimer. To make the reactions more efficient, they used a variety of catalysts like oxidized zirconium, iron, zinc, barium and aluminum. They found barium to be the most effective at increasing the yields for the styrene monomer in this reactor. Styrene monomer production peaked around 450 degrees Celsius, and after that temperature the dimer composition started to increase. Since the dimer is easier to separate, higher concentrations of more easily separatable materials may not be the most efficient outcome for the isolation of a pure stream of styrene monomer at the end of the separation process (Park et al., 2003).

Another type of reactor was a fluidized bed that also found 78% yields for the styrene monomer at 600 degrees Celsius. The primary source of material was polystyrene sourced from recycled packaging material. The range of temperatures that the pyrolysis streams were observed at was between 450 and 700 degrees Celsius. The experimental set up seen in Figure 2 shows a heating system that feeds into a fluidized bed reactor that is then condensed.
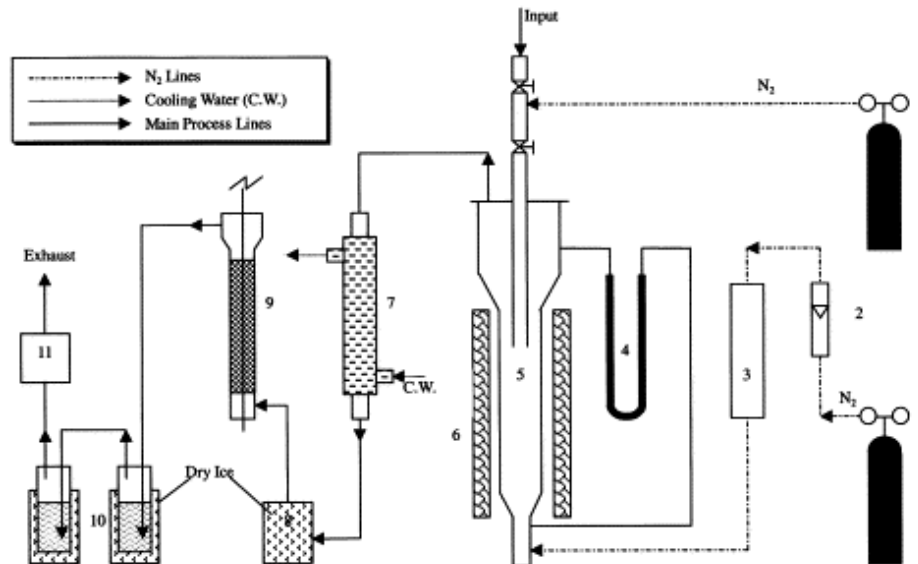
Figure 2. Fluidized bed reactor set up

At higher temperatures in the setup, more styrene monomer was produced due to a secondary reaction of the larger molecules being reduced down. There was in increase in the loss of total yield at higher temperatures due to the increased formation of more gas and coke. Waste streams from a potential distillation column could feed back into the pyrolysis reactor for a more efficient total yield (Liu et al., 2000).

Another type of fluidized reactor for pyrolysis reactions was a conical spouted bed reactor, shown in Figure 3, that achieved 64.5% yields of the styrene monomer at the 450 to 500 degrees Celsius range.

Figure 3. Conical spouted bed reactor diagram

This reactor uses sand as its fluidized material to negate the adhesiveness of the plastic particles as the melt. The spouted bed allowed for better heat transfer which is important for the endothermic pyrolysis reaction (Aguado et al., 2003).

Vapor Pressure models

For the products of a pyrolysis reaction, the properties of the products are not always readily available. In separation processes like distillation, vapor pressure and boiling points can determine t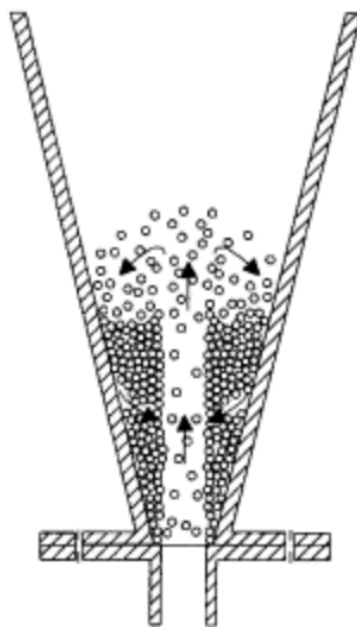he feasibility and difficulty in these separation processes. Due to a lack of concrete experimental data for the effluent streams of a pyrolysis reaction, there are ways to theoretically determine the physical properties of the components. There are a variety of different models on these physical components. Some model properties base estimations on factors like environmental conditions like temperature and pressure or look at the molecular properties.

Vapor pressure models are usually based off of the relationships between temperature and pressure and their subsequent effect on vapor-liquid equilibriums. One of the most basic models for vapor pressure is the Clausius-Clapeyron equation seen in Equation 1 (Myrdal & Yalkowsky, 1997).

$$ln\frac{P_1}{P_2} = \left(\frac{-\Delta H_{Vap}}{R}\right) * \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \textit{Equation 1}$$

The Clausius-Clapeyron equation can be used at a range of temperatures and pressures given the provided heat of vaporization for any chemical. Due to its wide range of use, it is not very accurate and there are many models which use the basis of the Clausius-Clapeyron equation but add more parameters to adjust for accuracy (I Brown, 2021).

The Myrdal method for estimating involves using an expanded version of the Clausius-Clapeyron equation and filling its subsequent parameters based on the molecular structure of molecules. The Hydrogen Bond Number (HBN), shown in Equation 2, is modeled on amount of alcohol, carboxylic acid, hydroperoxide and amines in a molecule.

$$HBN = \frac{\sqrt{OH+COOH}+0.33\sqrt{NH2}}{MW} \qquad \textit{Equation 2}$$

The effective number of torsional bonds is an important calculation, as seen in Equation 3, too because the mailability of the molecule can be a factor in its vapor-liquid equilibrium state.

$$\tau = \sum(SP3 + 0.5SP2 + 0.5RING) - 1 \qquad \textit{Equation 3}$$

These parameters make up the delta S and delta C in the expanded Clausius-Clapeyron equation. The Myrdal method of calculating vapor pressure does closely follow the experimental vapor pressure when used under certain parameters because of its precision to model vapor pressure based on the molecular structure. However, it does have a great deal of accuracy at modeling vapor pressure at more varied conditions like a high temperature above 500 degrees Celsius (Camredon & Aumont, 2006; Myrdal & Yalkowsky, 1997).

The Lee-Kesler method of modeling vapor pressure, as seen in Equation 4, is more accurate over a wider range of temperature because more of its parameters are based on environmental factors. Each of the variables, like temperature and pressure, in the equations are reduced and θ is

the ratio of boiling point over the critical temperature. The variable ω, as shown in Equation 5, is a variable that is designed to represent non-spherically shaped compounds called the Pitzer's acentric factor. Pitzer's functions are seen in Equations 6 & 7 and are the constants that were tuned with experimental vapor pressures.

$$ln\ (P_r^{Vap}) = f^0(T_r) + wf^1(T_r) \qquad\qquad\text{\textit{Equation 4}}$$

$$\omega = \frac{-ln(P_c)-f^0(\theta)}{f^1(\theta)} \qquad\qquad\text{\textit{Equation 5}}$$

$$f^0(T_r) = 5.9271 - \frac{6.09648}{T_r} - 1.28862 * ln\ T_r + 0.169347 * ln\ T_r^6 \qquad\text{\textit{Equation 6}}$$

$$f^1(T_r) = 15.2518 - \frac{15.6875}{T_r} - 13.4721 * ln\ T_r + 0.34577 * ln\ T_r^6 \qquad\text{\textit{Equation 7}}$$

To find the vapor pressure of a certain chemical using these equations, the boiling point, critical pressure and critical temperature are needed which can be found using the Joback method (Camredon & Aumont, 2006; Komkoua Mbienda et al., 2013)

The Joback method of estimating the physical properties is an older method dating back a few decades, but it is still an effective way of calculation. The Joback method estimates physical properties of the different functional groups and size of the molecule. Through empirical tests the effects of these different functional groups on various properties have been measured and are laid out in tables which can be used to calculate different viable parameters like critical temperature boiling point, and critical pressure. Many of these estimations rely on a base value that is additively changed by adding the value assigned by each functional group and the number of them. The different important functional groups are rings, non-rings, halogens, oxygens, nitrogens, and sulfur increments (Shi & Borchardt, 2017). Important determinable properties using the Joback method are boiling point, as seen in Equation 7; critical temperature, as seen in Equation 8; and critical pressure, as seen in Equation 9.

$$T_b = 198.2 + \Sigma \qquad\qquad\text{\textit{Equation 8}}$$

$$T_c = T_b\ /[0.584 + 0.965\ \Sigma - (\Sigma)^2] \qquad\qquad\text{\textit{Equation 9}}$$

$$P_c = (0.113 + 0.0032 * N_a - \Sigma)^{-2} \qquad\qquad\text{\textit{Equation 10}}$$

These equations provide the missing parameters needed for vapor pressure models like the Lee-Kesler and Myrdal equations.

Pyrolysis distillation

Distillation is the process of liquid separation by heating to form a vapor component that is condensed and a liquid component. It is usually done in a column that has an intake feed, a distilled outlet coming from the vapor, and the bottoms product from the remaining liquid. The

efficiency of the separation can be determined by the number of equilibrium stages in a column and the reflux ratio, which is the ratio at which the distilled liquid is fed back into the column.

The valuable products of a polystyrene pyrolysis stream are usually in liquid form, so it makes a relatively easy effluent stream to distill and potentially feedback into a pyrolysis reactor. The valuable product, the polystyrene monomer, is rather difficult to separate in one stage because there are waste products that have boiling points that are above, below, and very close to the styrene monomer. One of these products is ethylbenzene, which has a boiling point of 9 degrees Celsius away from the styrene monomer. Distillation can be done twice to remove both the products with higher boiling points in one column and lower boiling points in another. Additionally, there are some types of distillation that operate at very low pressure that can more precisely separate the styrene monomer to its needed purity of 99.6 for industrial streams (Liu et al., 2000).

Methodology

The following section outlines the procedures for carrying out the vapor pressure calculations and modeling the effluent distillation using the ASPEN Plus software.

Vapor Pressure Calculations

Different vapor pressure models were considered in Python: Myrdal, Lee-Kesler method, and Clausius-Clapeyron. The calculations were inputted and computed in Jupiter notebook, which is an open-source browser application that can share code. The mathematical package used for the calculation was NumPy, which is a terse and effective package for simple calculations. Plots and numerical physical constants were calculated using these tools.

Toluene was the initial compound used to test the different vapor pressure models for accuracy. Toluene was chosen because it is a well-studied compound that has vapor pressure plots readily available, and its physical constants are experimentally known. The constants for toluene were initially calculated with experimental values, but later were switched to the values calculated from the Joback method to make all the calculations more theoretical. The Lee-Kesler method was chosen as the model to model all of the vapor pressures for the effluent stream of a pyrolysis reaction because it was the most accurate at higher temperatures. This can be seen in Figure 4, which shows the different vapor pressures for toluene experimental data.
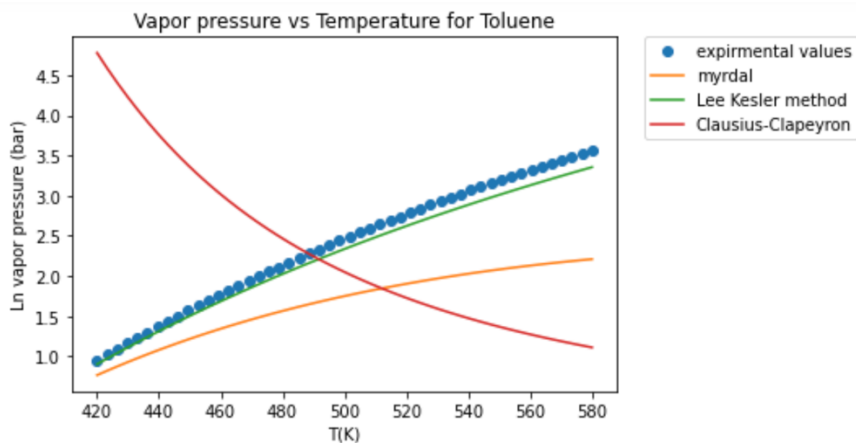
Figure 4. Vapor pressure plot vs temperature. Used to determine what vapor pressure model was used

The Lee-Kesler equation requires constants like the boiling point, critical temperature, and critical pressure to solve the associated equations to find vapor pressure. The Joback method was used to calculate these physical constants in Python for the resultant components of a pyrolysis reaction. Calculation of the Joback method was utilized in the summation of all the different components of the different types of bonds in each molecule. These calculations provided helpful incite to setting some of the parameters in our ASPEN simulations

ASPEN Simulation

The distillation of the effluent stream from a pyrolysis reactor was simulated using the ASPEN Plus simulation software. ASPEN Plus allows for a variety of chemical processes to be simulated, including distillations, separations, and reactor processes. Due to limitations within ASPEN regarding information for the heavy components, the simulation was run for the light components only. Therefore, the components in the distillation were the styrene monomer, toluene, benzene, ethylbenzene, and alpha-methyl styrene. The simulation was run at standard operating conditions (STP) using a predefined feed mixture based on the mass fraction for each component. Information regarding the feed conditions from ASPEN, including a table of the respective mass fraction of each component, can be seen in Figure 5.

Figure 5. Distillation Feed Conditions

The ASPEN simulation was conducted using the CHAO-SEA property method in order to simulate the process using Lee-Kesler enthalpy correlations. The distillation process was performed using two distillation columns modeled by the RadFrac distillation block. The RadFrac block was preferred over other, more simplified distillation blocks because it allowed for easier manipulation of process variables. Doing so made optimizing the process much easier and gave better insight on how different variables affect the products of the system. Both columns operated at STP with a molar reflux ratio of 0.3 and 40 trays within each column, respectively. The feed stream, defined by Figure 5, was fed into the first column to achieve the first separation of its components to potentially yield a highly purified styrene monomer. The initial feed stream had a mass flow rate of 100 lb/hr, as indicated in Figure 5. The respective feed streams for both of the columns entered the column above stage 10. The first distillation tower had a distillate mass flow rate of 30 lb/hr, and this distillate was sent out of the system as a waste stream. This waste stream contained about 76% styrene monomer, but it also yielded a large separation of other components, including about 20% toluene. Following the first distillation, the bottoms stream, which contained about 91% styrene monomer by mole at a mass flow rate of 70 lb/hr, was fed into the second

distillation column to purify the stream once more. This second distillation tower had a distillate mass flow rate of 10 lb/hr, yielding a product stream with an increasingly pure concentration of styrene monomer and the remaining components resulting in waste. Figure 6 displays the main flowsheet for the ASPEN simulation.
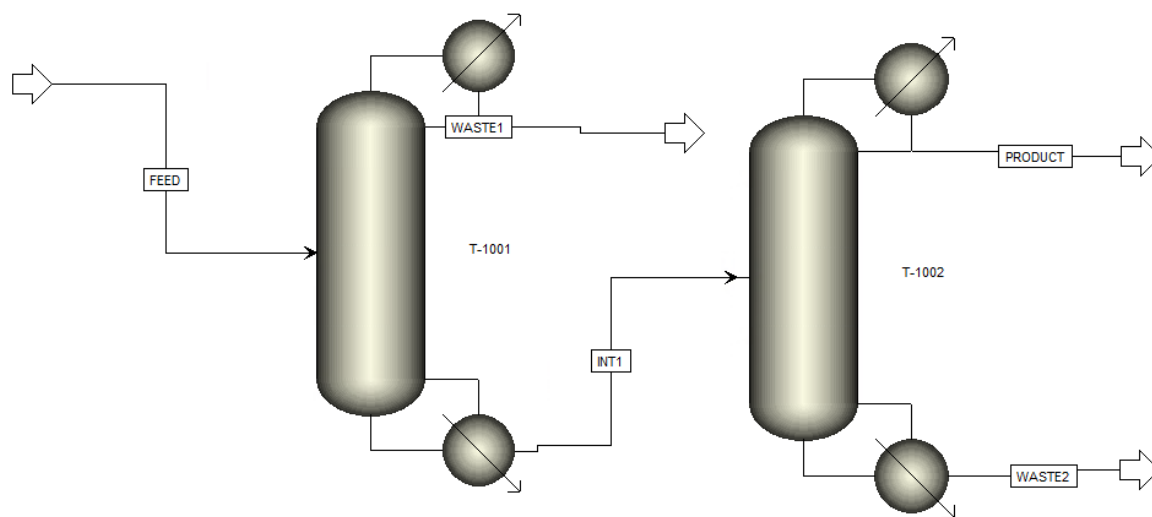

Figure 6. Process Flow Diagram

Using the results from our specified simulation, we then ran several test runs using varying amounts of styrene monomer in the feed stream. The different values for the feed and product concentration were recorded, as well as the reboiler duty in the system to perform the distillation. Based on this data, we used a graphical analysis to find the optimal feed concentration of styrene monomer to yield the most amount of product while using the least amount of energy. Additionally, we showed the relationship between the feed concentration and the tower reflux ratio to find the optimal feed and reflux in order to yield the most amount of product at our specified operating conditions. We believe this information will be especially useful for future simulations on this topic.

Results and Discussion

We first we calculated the physical constants for the pyrolysis stream components using Python. Then we used ASPEN to simulate the separation of these compounds in a distillation column.

Vapor Pressure

The boiling points for the molecules in the pyrolysis product stream calculated with the Joback Method are shown in Table 1. The calculated values for all of the values are all close and show a distinct difference between the heavy components in the streams and the light components in the streams. These differences are highlighted in the table.

Table 1. Table of boiling points for pyrolysis reactants. Lights stream is highlighted

	Theoretical boiling point (K)	*Experimental boiling point (K)*
Toluene	382.15	383.7
Benzene	307.28	353.2
α-Methylstyrene	425.0	439.1
Monomer	427.63	418.1
Dimer	601.86	
1,2-Diphenylethane	582.42	557.1
Trimer	756.1	

The Joback method seems to calculate the molecules with simple structure better. This is potentially because the intermolecular forces are harder to account for on things like a double bond and the ways that they interact with each other. Benzene is a notable exception, which has a much lighter theoretical boiling point because it is too simplistic, causing the model to under-calculate its boiling point. Values for the Dimer and Trimer of styrene are not readily known which is why it is important to model them in this sense. Given the accuracy of the other calculated temperatures, the boiling points should only be 10-20 degrees off from calculated.

The Vapor pressure plot shown in Figure 7 shows the correlation between increasing vapor pressure and increasing temperature. It was plotted with values calculated with the Lee Kesler method based on the physical constants: critical pressure, critical temperature, and the boiling point calculated above.
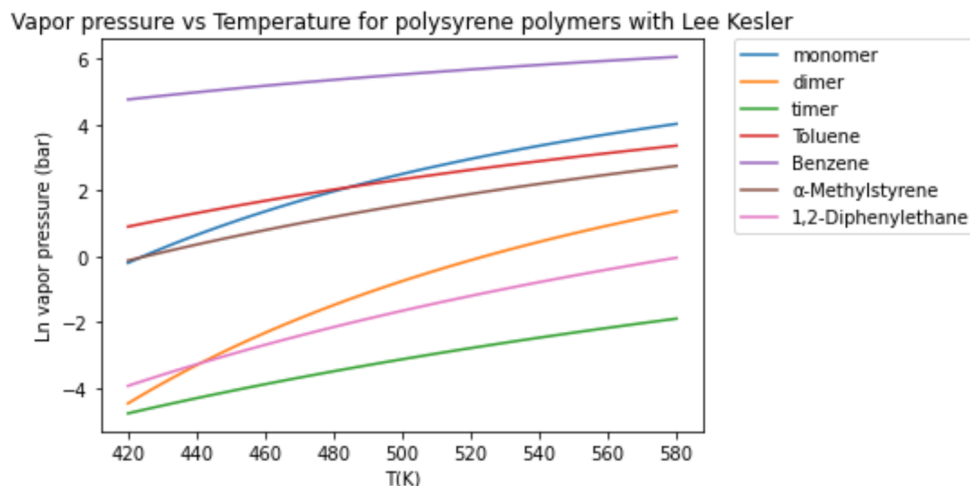
Figure 7. Plot of vapor pressures vs temperature for the different reactants of a pyrolysis stream.

The plot also shows large differences between the light, the styrene monomer, benzene, toluene and a-methylstyrene and heavy components, the 1,2-diphenyl ethane and the styrene dimer and trimer. The higher range of the vapor pressures from the styrene dimer and trimer indicates that the separation process would be straight-forward and could potentially just be flashed before entering the distillation column feed stream. The plot indicates that the vapor pressure lines that are closes to each other are the most difficult to separate thus the separation process for toluene, a-methylstyrene and the styrene monomer will be more difficult than the separation of benzene.

Aspen Results

The results of the ASPEN simulation were based on the most optimal run we were able to achieve using our specified conditions. Table 2 summarizes our results, with the focus being on the final concentration of styrene monomer that we yielded from the process in addition to the product flow rate. The simulation resulted in a 10 lb/hr product stream that is 93.6% styrene monomer by mole.

Table 2 ASPEN Stream Results

	Units	FEED	INT1	PRODUCT	WASTE1	WASTE2
+ Mole Flows	lbmol/hr	0.959457	0.665629	0.0954974	0.293828	0.570131
− Mole Fractions						
STYRE-01		0.863226	0.911788	0.93695	0.753215	0.907574
TOLUE-01		0.0561758	8.8662e-07	2.51024e-06	0.183433	6.14662e-07
ALPHA-01		0.0537305	0.0694675	0.0363221	0.0180803	0.0750194
BENZE-01		0.0021036	2.90745e-17	0	0.00686902	0
ETHYL-01		0.0247639	0.0187432	0.026725	0.0384028	0.0174063
+ Mass Flows	lb/hr	100	70	10	30	60

Using data from multiple runs using varying styrene monomer feed rates, the following graphs were designed to display optimal operating conditions for possible future distillations. Reboiler heat duties were gathered from ASPEN using the model results. The original reboiler heat duty data was recorded in BTU/hr, but the data was converted to MJ/kg so that the data may be easily compared to data on other common fuels. Figure 8 displays the relationship between the feed concentration of styrene monomer with the product concentration and the reboiler heat duty. Figure 9 displays the relationship between the feed and product concentrations with the reflux ratio of the towers.
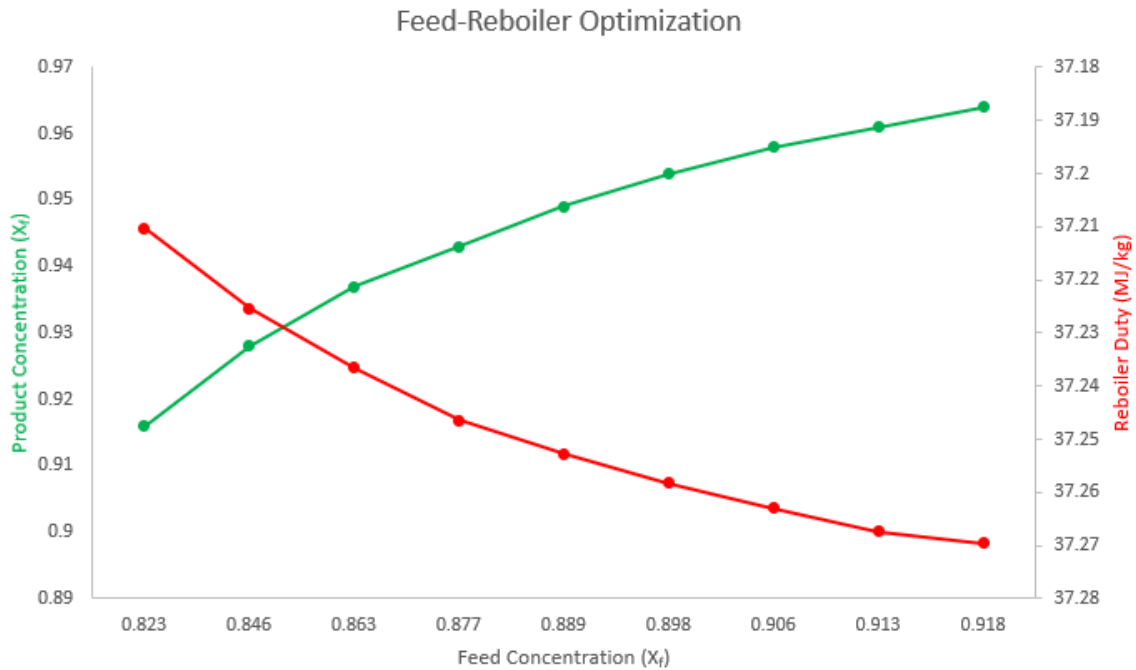

Figure 8. Graph of the relationship between the feed concentration of styrene monomer to the product concentration (mol fraction) and reboiler duty (MJ/kg). The feed concentration at the intersection point (0.85,0.93,37.23) is the mole fraction of styrene monomer in the feed.
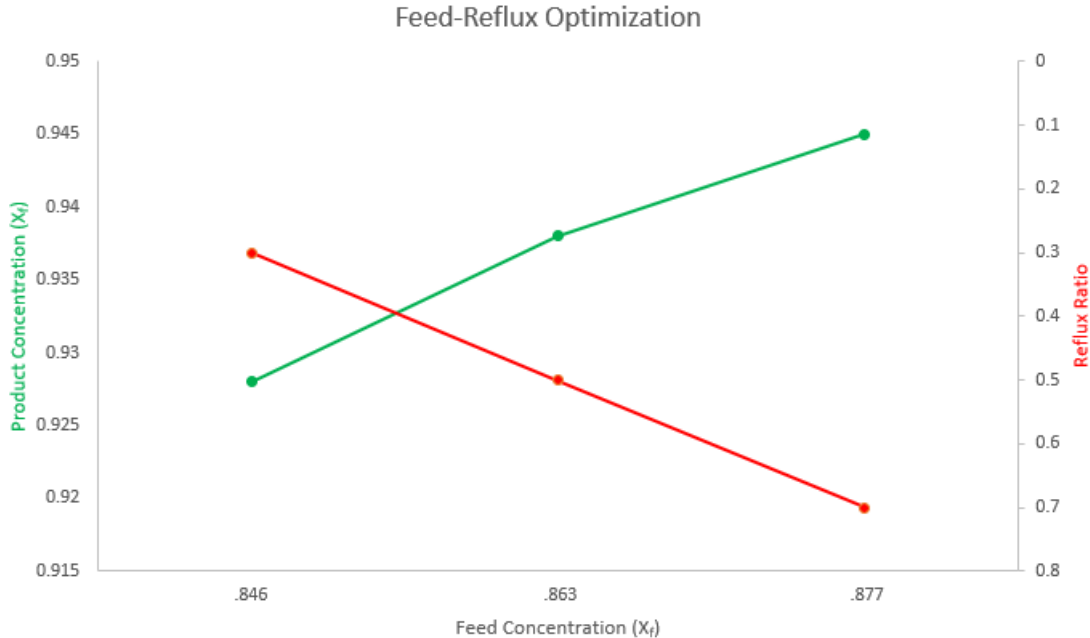
Figure 9 Graph of the feed concentration of styrene monomer to the product concentration (mol fraction) and tower reflux ratio. The feed concentration and reflux ratio at the intersection point (0.85,0.9325,0.401) yields the highest possible product at our operating conditions.

A large amount of material was not recovered from the system in this simulation, and this ultimately yielded a large quantity of waste in the simulation. Ideally, these streams would be captured and recycled within the system to yield the most styrene monomer possible from the feed. However, the ASPEN solver could not properly solve for the correct stream data when a recycle stream was added to the process. Information was manually inputted for the miscalculated streams as an attempt to rectify the issue, but the ASPEN solver continued to yield errors while running the simulation. Although the addition of a recycle stream to the process would yield the most accurate results when compared to a possible large-scale industrial process, the simulation was ultimately performed without the recycle stream due to this limitation. Therefore, the simulation results in a lower overall yield of the styrene monomer and therefore may not be as highly purified compared to what may be achievable in an industrial setting.

Using the information from Figure 8, the reboiler duty required to perform the distillation remains steady at around 37 MJ/kg, with the optimal reboiler duty being around 37.23 MJ/kg. Compared to other common fuels, the heat value for this process is lower compared to some other common fuels. For example, methane and natural gas typically have heat values around 50-55 MJ/kg, and other fuels like diesel, gasoline, and crude oil have heat values around 42-46 MJ/kg. Based on this information, the styrene monomer is not as effective as a fuel compared to other common fuels. However, given the possibility for this process to be both more economically and environmentally beneficial than the production of other fuels, the heat value is useful information to compare the pros and cons of this process.

Conclusions and Recommendations

The research has shown that it is possible for the use of a distillation column for the separation of the styrene monomer from the effluent flow in a pyrolysis reactor. The experimental distillations in ASPEN focused especially on the distillation between the lighter compounds in a pyrolysis stream since the heavier part of the stream is more easily separated. The lighter stream products have very similar physical properties that are important for separation in distillation columns like boiling point and vapor pressure.

For the distillation of the lights streams, the data indicates that there is a balance between the operating costs and the amount of styrene monomer composition distilled. Operating costs are an important factor in the process of polystyrene pyrolysis and distillation, because the end product, styrene monomer, should be competitive in price with of freshly produced styrene to help reduce total necessary plastic production. The results of the ASPEN simulations show that these optimal values are reached around a reflux ratio of 0.4 and a feed composition of 85% monomer.

The composition of a styrene monomer exiting a pyrolysis reactor is not necessarily 85% composition and are usually a few percentage points lower, but the reactor could be altered to produce a better styrene composition. This could potentially cause more coking in the reactor but could be made up by the fact that it is coming into our distillation at the ideal feed composition. Another simple approach would be to have a simple flash separator that could easily bring up the styrene composition because the heavy stream could be easily removed.

On the other end of our distillation column at the distillation product stream, the column produces styrene monomer at a composition of around 93% with the optimal operating costs. 93% styrene monomer is not that useful on its own and cannot be sold on the market at that purity, but the distillation column set up in the idealized operating conditions allows for the most reasonable production of it at that purity. Styrene monomer used for industrial polymerization usually requires a purity of the styrene monomer to be 99.6% pure. To achieve this purity, the distillation described by our research would require another step after the column.

The largest difficulty of styrene monomer separation is the removal of the ethylbenzene that is formed alongside the styrene in the pyrolysis reactor. Since both molecules have a close boiling point, the separation process is difficult to simulate in ASPEN. Studies using experimental data and distillation columns with pyrolysis often use specific environments like vacuum distillation, which is not easily to replicate with ASPEN.

The distillation column set-up with ASPEN was also not able to utilize helpful systems of designs like recycling streams. In the current process, the bottoms product from the second distillation column has a composition than higher feed of the first. If this stream was recycled back, it would not only improve the styrene yield of the total stream, but it would also likely improve the composition of styrene in the final distillation. Additionally, the process as a whole could benefit from more recycled streams such as the initial flash before our column and potentially the distillate product, which could be fed back into the polystyrene feed entering the pyrolysis reactor. Even in the event that they are not able to be broken down, additions of the

smaller, less useful molecules like alpha-methyl styrene being present in the reaction can force the equilibrium in the direction to reduce the creation of these molecules, thus increasing the total styrene yields in the reactor.

The next steps for this research would be to test some of these designs in actual distillation columns to determine whether the feed compositions and the reflux ratios. The simulation software, ASPEN, is not able to determine the potential reactor mechanism happening inside the column at elevated temperatures, and it could be possible that More efficient compositions of the styrene monomer could be obtained if some slow pyrolysis happened inside the column. Expanded experiments should include recycle streams. Experimental tests run congruently with simulations guiding the parameters can produce a valuable result towards the efficient recycling of polystyrene.

References

Aguado, R., Olazar, M., Gaisán, B., Prieto, R., & Bilbao, J. (2003). Kinetics of polystyrene pyrolysis in a conical spouted bed reactor. *Chemical Engineering Journal*, *92*(1–3), 91–99. https://doi.org/10.1016/S1385-8947(02)00119-5

Camredon, M., & Aumont, B. (2006). Assessment of vapor pressure estimation methods for secondary organic aerosol modeling. *Atmospheric Environment*, *40*, 2105–2116. https://doi.org/10.1016/j.atmosenv.2005.11.051

Hassan, E. B., Elsayed, I., & Eseyin, A. (2016). Production high yields of aromatic hydrocarbons through catalytic fast pyrolysis of torrefied wood and polystyrene. *Fuel*, *174*, 317–324. https://doi.org/10.1016/j.fuel.2016.02.031

I Brown, O. L. (2021). *THE CLAUSIUS-CLAPEYRON EQUATION* (Vol. 19). UTC. https://pubs.acs.org/sharingguidelines

Komkoua Mbienda, A. J., Tchawoua, C., Vondou, D. A., & Mkankam Kamga, F. (2013). Evaluation of Vapor Pressure Estimation Methods for Use in Simulating the Dynamic of Atmospheric Organic Aerosols. *International Journal of Geophysics*, *2013*, 13. https://doi.org/10.1155/2013/612375

Kruse, T. M., Sang Woo, O., & Broadbelt, L. J. (2001). Detailed mechanistic modeling of polymer degradation: Application to polystyrene. *Chemical Engineering Science*, *56*(3), 971–979. https://doi.org/10.1016/S0009-2509(00)00312-2

Kruse, T. M., Woo, O. S., Wong, H. W., Khan, S. S., & Broadbelt, L. J. (2002). Mechanistic modeling of polymer degradation: A comprehensive study of polystyrene. *Macromolecules*, *35*(20), 7830–7844. https://doi.org/10.1021/ma020490a

Liu, Y., Qian, J., & Wang, J. (2000). Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction. *Fuel Processing Technology*, *63*(1), 45–55. https://doi.org/10.1016/S0378-3820(99)00066-1

Myrdal, P. B., & Yalkowsky, S. H. (1997). Estimating pure component vapor pressures of complex organic molecules. *Industrial and Engineering Chemistry Research*, *36*(6), 2494–2499. https://doi.org/10.1021/ie950242l

Park, J. J., Park, K., Kim, J. S., Maken, S., Song, H., Shin, H., Park, J. W., & Choi, M. J. (2003). Characterization of Styrene Recovery from the Pyrolysis of Waste Expandable Polystyrene. *Energy and Fuels*, *17*(6), 1576–1582. https://doi.org/10.1021/ef030102l

Shi, C., & Borchardt, T. B. (2017). JRgui: A Python Program of Joback and Reid Method. *ACS Omega*, *2*(12), 8682–8688. https://doi.org/10.1021/acsomega.7b01464

Student Energy. (n.d.). *Pyrolysis*. Retrieved May 4, 2021, from https://studentenergy.org/pyrolysis/

Appendices

Appendix A: List of Acronyms

Table 3 Glossary of acronyms used throughout this report

Name	Meaning
COOH	Carboxylic acid
$-\Delta H_{Vap}$	Delta Enthalpy of Vaporization
$f^0 \& f^1$	Pitzer's functions
HBN	Hydrogen Bond Number
MW	Molecular Weight
NH2	Amino Radical
OH	Hydroxide
P	Pressure
Pc	Critical Pressure
Pr	Reduced Temperature
R	The universal Gas Constant
RING	Number of rings
SP2	One S and 2 P orbital are Hybridized
SP3	One S and 3 P orbital are Hybridized
T	Temperature
Tb	Boiling Point
Tc	Critical Temperature
θ	The ratio of boiling point
Tr	Reduced Temperature
τ	Effective number of torsional bonds
ω	Pitzer's acentric factor

Appendix B: Vapor Pressure Python Calculations

```
import numpy as np
%matplotlib inline
import matplotlib.pyplot as plt

psi=[2.60,3.12,3.73,4.42,5.22,6.12,7.15,8.31,9.62,11.08,12.71,14.52,14.70,16.53,18.75,21.20,23.
88 ,26.82 ,30.03 ,33.52 ,37.32 ,41.44,45.90,50.71]
c=np.repeat(6.89476,24)
monoP=np.log(psi*c)
monoT=np.linspace(90+273.15,200+273.15,24)
#print (Kpa)
plt.plot (monoT,monoP)

# Joback method, attempts to calculated TB for monomor
#      tc      pc       tb
# -Ch3, 0.0141   -0.0012   23.58
#=ch-  0.0082   0.0011    26.73
#CH2   0.0189     0      18.18
# =C<   0.0117     0.0011     24.14
# >CH−   0.0122    0.0004       21.74
# −CH2−  0.0189    00.      22.88
c2h=26.73
c=24.14

Tci=2*0.0189+7*0.0082
Pci=7*0.0011
Na=16

Tb = 198.2+18.18+7*c2h+c*1

Tc=Tb*((0.584+0.965*Tci-(Tci)**2)**-1)
Pc=(0.113+0.0032*Na-Pci)**-2
print('Tb,Pc,Tc')
print(Tb,Pc,Tc)

# myrdal
#HBN=Root(oh+COOH)+ 0.33Root(NH2)all over mass
#tau=sum()
sp3=4
sp2=4
```

```
ring=1
tau=sp3+0.5*sp2+0.5*ring-1
HBN=0
Pvap1= (((-21.2+0.3*tau+177*HBN)*((Tb-T)/T))+(10.8+0.25*tau)*np.log(Tb/T))
print(Pvap1)
#values are not actually that off.

#Lee Kesler method, we still need some of the values in here for now???
Tr=T/Tc
Trc=Tb/Tc
print (Tr)
f00=5.92714-(6.09648/Trc)-1.28862*np.log(Trc)+0.169347*np.log(np.power(Trc,6))
f10=15.2518-15.6875/Trc-13.4721*np.log(Trc)+0.43577*np.log(Trc**6)

f0=5.92714-(6.09648/Tr)-1.28862*np.log(Tr)+0.169347*np.log(np.power(Tr,6))
f1=15.2518-15.6875/Tr-13.4721*np.log(Tr)+0.43577*np.log(Tr**6)
#pressure in bars here
w=-(np.log(Pc)+f00)/f10
# old way
#w=-np.log10(Pc)

PvapL1=np.log((np.exp(w*f1+f0))*Pc)
print ('w')
print(w)
print ('f0')
print (f0)
print ('f1')
print (f1)
print ('pvap')
print (Pvap1)

plt.plot (T,PvapL1,label="monomer")
#plt.plot (T,PvapT,label="monomer exp")
plt.plot (T,PvapL2, label="dimer")
plt.plot (T,PvapL3,label="timer")
plt.plot (T,PvapL4,label="Toluene")
plt.plot (T,PvapL5,label="Benzene")
plt.plot (T,PvapL6,label="α-Methylstyrene")
plt.plot (T,PvapL7,label="1,2-Diphenylethane")
plt.legend(bbox_to_anchor=(1.05, 1), loc=2, borderaxespad=0.)
```

plt.xlabel('T(K)')
plt.ylabel('Ln vapor pressure (bar)')
plt.title ('Vapor pressure vs Temperature for polysyrene polymers with Lee Kesler')