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SEPARATION AND PURIFICATION OF AROMATICS FROM CRACKED CROP OILS USING SULFOLANE

by

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Bachelor of Science, University of Tehran, 2009

A Thesis
Submitted to the Graduate Faculty

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in partial fulfillment of the requirements

for the degree of

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This thesis, submitted by Nahid Khatibi in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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This thesis meets the standards for appearance, conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

Wayne Swisher

Wayne Swisher

Date

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Title Separation and Purification of Aromatics from Cracked Crop Oils Using Sulfolane

Department Chemical Engineering

Degree Master of Science

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Date 07/30/2012

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ABSTRACT

Aromatics, such as benzene and toluene, are important for the production of many materials such as polystyrene and other polymers. Benzene and toluene are, most commonly produced from crude oil. But due to the depletion of petroleum resources, the world is looking for renewable alternatives.

Studies of the catalytic cracking of triacylglycerol containing oils (TAG), such as soybean oil, have demonstrated that a high concentration of aromatics can be produced under certain conditions. This discovery provides an opportunity to develop a pathway for the production of aromatics from renewable resources. The main focus of this research was to develop the process conditions that are required to recover aromatics from cracked soybean oil using sulfolane as a solvent and to outline the process steps necessary for recovering and purifying the target aromatics from the solvent. To achieve these objectives, simulations and experiments were performed. The primary objective of this thesis was to find the optimum conditions for the maximum extraction yield. Another objective was to estimate the overall cost of a viable process.

Using 20 mL test tubes, lab scale screening experiments were performed, and two major variables were investigated by using full factorial statistical design experiments. The two variables were the temperature of the mixer vessel and the solvent to solute ratio. Other variables, such as initial pressure, stirring rate, feedstock quantity, and residence-time, were kept constant. The predicted variables that were used to determine the optimal operating conditions were fraction of fatty acid solute extracted by the sulfolane solvent and the quality of the chemical compositions of the final product. Gas Chromatographic (GC-MS) analysis was used to identify and quantify the chemical composition of the samples.

The range of 3-to-1 to 11-to-1 ratio of sulfolane to BTEX present in the distilled crackate was explored. The optimum yield was found to occur at the 9-to-1 ratio of solvent-to-solute and higher. The optimum temperature was concluded to be 50°C among three temperatures of 30°C, 50°C and 70°C. The recovery of benzene and toluene in the LLE process were determined to be around 80% and 70%, respectively for a single stage extraction. It was calculated that a 3-stage extraction system will result the 99.5% recovery for benzene and toluene. The best purification scheme (of 3 studied) was, three columns in series with the column 1 light key being benzene, column 2 light key toluene, and column 3 heavy key sulfolane. The slightly greater NPV@12%, $31 million, and DCFROR, 33%, belonged to this configuration.

1. INTRODUCTION

It has been reported that the world's petroleum resources will be depleted within the next 50 years [52]. For that reason the world is looking for renewable alternative sources to replace petroleum [8]. Transportation fuels, petrochemicals, and polymers are some examples where renewable alternatives are needed. Previous research at UND has shown that crop oils can be cracked to make a petroleum replacement that is useful for fuel production [51]. Modifications to the process could be used to derive many valuable products for everyday use, including nylon, synthetic rubber (SBR), glues, and fibers in clothing. These products and many others are produced from aromatics. This project involves the isolation and purification of aromatics from thermally cracked crop oils so that they may replace their petroleum analogs.

The oils and fats of vegetables and animals have been the most common renewable feedstock of the chemical industry [5, 6]. The estimate of the annual global production of the main vegetable oils from different plants, such as palm, soy, rapeseed, cotton, peanut, sunflower, palm kernel, olive, and coconut amounted to 84.6 million tons (Mt) in 1999/2000 and increased to 137.3 Mt in 2009/10 (an increase of 62 %) [15].

The controversial topic of using crop oil as food vs. fuel has existed for years. Traditionally, oil and fat consumption was shared between food, feed, and industrial use in the ratio 80:6:14. But with growing production of biodiesel this ratio is probably now closer to 74:6:20 [18]. It was recently shown that biomass can be produced in a volume sufficient for industrial utilization without compromising the food supply for the increasing global population [36]. With that being said there are many reasons that justify crop oil usage development such as [63]:

- A market for excess production of vegetable oil and animal fat is provided.
- The nation's dependence on imported petroleum will be reduced.
- The source is renewable.
- The source does not contribute in global warming due to its closed carbon cycle.
- Emerging non-edible crop oils can be grown on marginally productive lands.
- Emerging bacteriological and algal technologies allow TAGs to be generated from other non-crop oil sources.

Crop oil has been used as an alternative energy resource since 1900. Most crop oils are water-insoluble, hydrophobic substances referred to as triglycerides (TAG) [32]. Figure 1 shows a typical TAG molecule. The TAG molecule has a glycerol "backbone" where three fatty acids (FAs) are attached to it. These FAs are different by the length of the carbon chains, also the number, orientation, and position of double bonds in these chains [58].

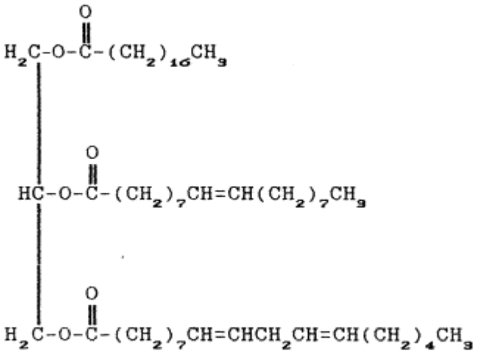

Figure 1 Structure of a typical triglyceride molecule.

Thermal decomposition of TAG oils produces compounds classified as alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Figure 2 illustrates a schematic for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from the thermal decomposition of TAG oils [58].

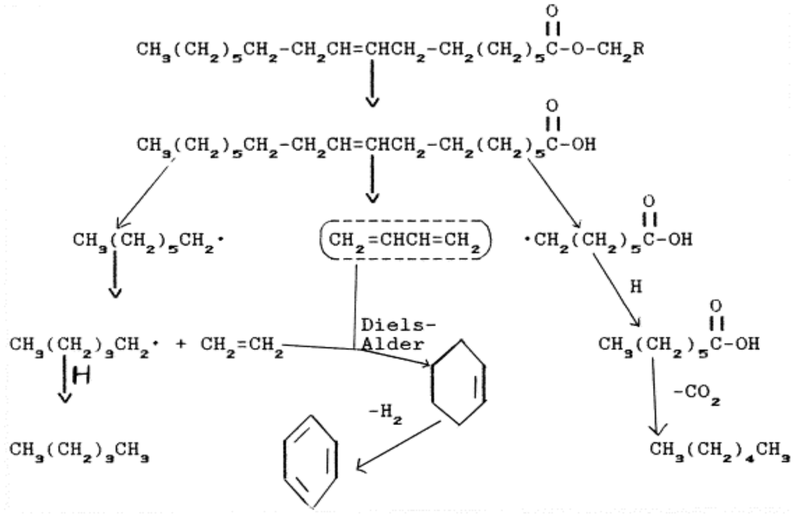

Figure 2 Thermal decomposition mechanisms.

Aromatics are ring shaped organic compounds exclusively composed of the elements carbon and hydrogen. They are commercially produced from petroleum. The main aromatics are benzene, toluene, o-xylene, p-xylene, and m-xylene, known collectively as BTX.

Products made from aromatics are common in society. Well known examples include aspirin, air-bags, and high-tech CDs. Aromatics are vital as raw materials for many polymers such as, polystyrene, polyurethane [25, 46, 69], and synthetic fibers. These are durable, safe, comfortable and lightweight [20, 45].

Benzene is the simplest aromatic with a ring of 6 carbon atoms and 6 hydrogen atoms. It is not used directly by consumers but is an important raw material for the manufacture of a great number of other chemicals (intermediates) such as styrene, cyclohexane, cumene, and alkyl-benzene [46]. These chemicals are then used as feedstock to produce polystyrene, synthesis rubber (SBR), Nylon, aspirin, penicillin, surfactants, etc.

Toluene is composed of 7 carbon atoms and 8 hydrogen atoms. It is used widely as the starting material for the manufacture of industrial chemicals. Toluene is found in solvents, paints and glues [27], and in gasoline (as an octane booster) [52]. A major polymer manufactured from toluene via toluene diisocyanate (TDI) is polyurethane [25], used as a foam in furniture, mattresses, car seats, and building insulation, and in coatings for floors, furniture and refrigerators, sports equipment, etc. [25, 46, and 47].

Xylenes are liquids composed of 8 carbon atoms and 10 hydrogen atoms. There are three different xylenes which are often mixed when produced: para-xylene, ortho-xylene, and metha-xylene. Para-xylene is the most commercially important. It is used to make polyesters. The most widely-used polyester is polyethylene terephthalate (PET) which is used in lightweight recyclable soft drinks bottles and for fibers in clothing. It can also be made into a film which is used in video tapes, audio tapes and x-ray films.

Thermal cracking of the TAG oil breaks the long chain fatty acids present in the oil into shorter chain molecules such as alkanes, and also into aromatics [22, 28, 31, 32, 48, 55 - 57]. The UND process to generate aromatics by the catalytic cracking of TAG oils is described elsewhere [7, 24, and 51].

Using zeolite catalysts in the cracking process of crop oils improves aromatics' yield and may be a promising technology for the production of the aromatics. The selectivity of zeolites for aromatics production depends on acidity levels, pore size, dopant concentration and cracking temperature. HZSM-5 has been shown to have the maximum selectivity to aromatics among the zeolites [2, 7, 23, and 42].

The separation of aromatic and aliphatic hydrocarbon mixtures is challenging due to the overlapping range of boiling points of the selected compounds. Several combinations of aromatics and alkanes also form azeotropes. Processes that have been studied for the separation of aromatics from aliphatic hydrocarbon mixtures include: liquid extraction, suitable for the range of 20–65 wt. % aromatic content [14], extractive distillation for the range of 65–90 wt. % aromatics [9, 29], and azeotropic distillation for high aromatic content, >90 wt. % [35].

Solvents used for liquid extraction require high selectivity for aromatics, high capacity, the capability to form two phases at reasonable temperatures, the capability for rapid phase separation, easy regeneration, and good thermal stability. They should also be non-corrosive and non-reactive [33].

Sulfolane, the common name for tetrahydrothiophene-1,1dioxide, was developed by the Shell Oil Company in the early 1940s and is still the most efficient solvent available for the extraction of aromatics from a mixed aromatics/aliphatic hydrocarbon stream. It is used in industry throughout the world [13, 64-68].

Some of the benefits of using sulfolane as the solvent are:

- Sulfolane is a readily available commodity chemical.
- There are no co-solvents or proprietary additives required.
- Sulfolane does not contain nitrogen which can be harmful to catalysts in downstream processes.
- Sulfolane is highly soluble in water.
- Sulfolane can be efficiently recovered and reused [11, 14, 19, 35, and 60].

The most common version of the sulfolane process can be licensed from Honeywell/UOP (Universal Oil Products). It uses liquid-liquid extraction followed by distillation to recover high purity aromatics from hydrocarbon mixtures, such as reformed petroleum naphtha (reformate), pyrolysis gasoline (pygas), or coke oven light oil (COLO) as shown in Figure 3. This process is leading the market by continually improving the process technology, catalysts, and adsorbent [62].

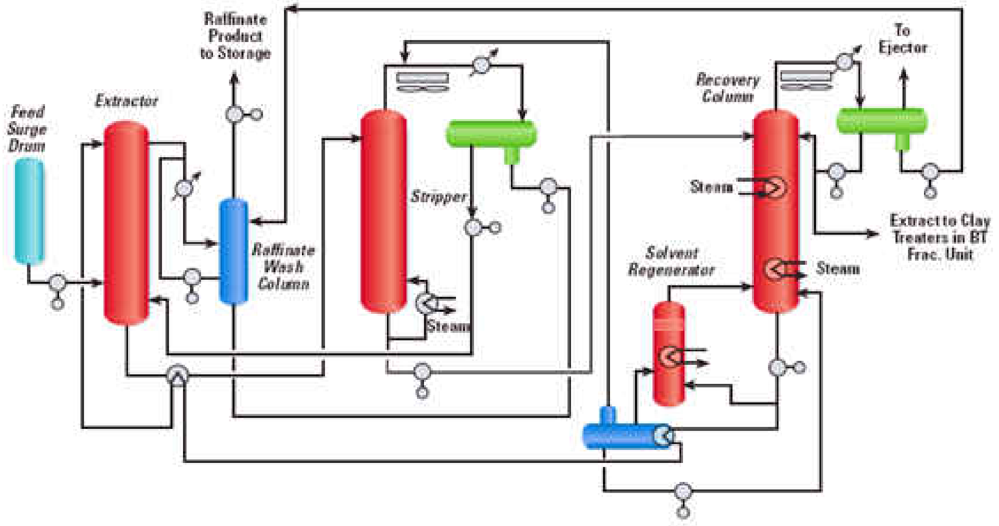

Figure 3 Schematic of sulfolane process by UOP.

Recently updated information provided by the company on their website shows that the UOP Extractive Distillation (ED) Sulfolane™ process uses sulfolane solvent for the recovery of high purity benzene and toluene products from petroleum reformate splitter overhead stream. The process offers [62]:

- 99.9 wt-% purity benzene (ASTM Refined Benzene-545)
- High purity toluene with less than 1000 wt-ppm non-aromatics.
- Benzene and toluene recovery greater than 99.5%
- Low solvent consumption
- Maximum energy efficiency

The main focus of the current work was to develop the process conditions that are required to recover the aromatics from the cracked oil product. In this project sulfolane was used as the solvent to develop a model to evaluate the extraction yield, recovery and purification procedure for the target aromatics; benzene and toluene. Solvent regeneration was also modeled to find the optimum conditions for separating benzene, toluene, and sulfolane from the rest of ethylbenzene, o-xylene, p-xylene, and cumene. The overall process conditions and costs were then estimated. What makes this work unique is the feedstock that has been used. While previous work used petroleum feedstock, this work is based on cracked crop oil.

This thesis is represented in two main chapters: chapter 2 includes the Liquid Liquid Extraction section of the project, which was done in the lab. Chapter 3 is the purification process which was conducted by modeling three different process configurations to find the optimum conditions for the aromatics purification and solvent regeneration portion of the process. Chapter 3 also provides the economic analysis of the overall process. Finally in chapter 4 the conclusions are presented and future work is suggested in chapter 5. Appendices are included for further information at the end.

2. AROMATICS EXTRACTION BY SULFOLANE

2.1. Background

Liquid–liquid extraction, also known as solvent extraction or solvent partitioning, is a method to separate compounds based on differences in their relative solubility in two different immiscible liquids. It is an extraction of substances from one liquid phase into another liquid phase. The following parameters need to be evaluated when optimizing the design and operation of the extraction processes:

1) Solvent selection
2) Operating Conditions - Depending on the nature of the extraction process, the temperature, pH and residence time can affect the yield and/or selectivity.
3) Mode of Operation - Extractors can be operated in crosscurrent or counter-current mode.
4) Extractor Type - Commercially important extractors can be classified into the following broad categories;
    - Mixer-Settlers
    - Centrifugal devices
    - Column contactors (static) - Examples include spray columns, trayed columns, and packed columns.
    - Column contactors (agitated)-Agitated columns can be further split into rotary or reciprocating type. Examples of rotary agitated columns include rotary disc

contactors, Scheibel columns, and Kuhni columns. Examples of reciprocating agitated columns include the Karr column and the pulsed column.

5) Design Criteria - The basic function of extraction equipment is to mix two phases, form and maintain droplets of the dispersed phase, and later separate the phases.

- Mixing- The amount of mixing required is determined by physical properties such as viscosity, interfacial tension and density differences between the two phases
- Settling - The settling characteristics depend on fluid properties (density difference, interfacial tension, and continuous phase viscosity) and the amount of mixing. Settling in agitated batch vessels is carried out by stopping the agitator. In continuous columns, a settling section is provided either as a part of the extractor or as a separate piece of equipment downstream of the extractor.
- Selection of Continuous and Dispersed Phase - In column extractors, the phase with the lower viscosity (lower flow resistance) is generally chosen as the continuous phase. Also note that the phase with the higher flow rate can be dispersed to create more interfacial area and turbulence.

The organic liquid product (OLP) from thermally cracked soybean oil contains long chain aliphatics and fatty acids, as explained in chapter 1. Thermal cracking is one of the main processes in the petroleum industry. It involves breaking up larger carbon chains molecules into smaller ones to produce more desirable and valuable products by using high pressure and/or high temperature [32]. It is difficult to achieve high purity aromatics using ordinary distillation operations because of the formation of binary azeotropes with aliphatics. Thus extraction was used to separate the aromatics from aliphatics. To purify the target aromatics, a distillation-based process is typically used in industry.

2.2. Literature Review

The recovery of aromatics from petroleum feedstock has been studied for decades [4, 11, 14, and 29]. The most common way to separate the aromatics from aliphatic hydrocarbons in industry is using a solvent and extracting the aromatics from the mixture. [13, 62, 64-68].

Some of the common solvents that have been used to extract aromatics from petroleum feedstock are: sulfolane [10, 33, 41], ethylene carbonate [38], N-Formylmorpholine (NFM) [21], glycols [38, 40], and ionic liquids [17, 36, 44]. Huang et al. used a Rose-Williams VLE device to recover aromatics using N-Formylmorpholine (NFM) as the solvent [21]. The selectivity of three different solvents, tetramethylene sulfone (i.e., sulfolane), dimethyl sulfoxide (DMSO), and ethylene carbonate, were compared by Mohsen-Nia et al for separation of toluene from alkanes at three temperatures ranging from 25 to 40 °C [39]. Other solvents have also been used or researched. Recently, ionic liquids have been getting attention. Details of historical solvents used in various extraction processes are shown in Table 1 [43].

The most important characteristics in an extractive solvent are the relative miscibility and the selectivity for targeted compounds. Other characteristics such as chemical stability, availability, compatibility, price, and environmental hazards also must be taken into account. Besides the high efficiency of sulfolane, its boiling point allows comparatively easy separation of the sulfolane from the extract [43].

Different extractor designs have been used for extracting aromatics from hydrocarbons including rotating disk contactors (RDC) and trayed contactors. Studies have shown that multiple stage extraction yields the best results. Deal et al. studied the recovery of aromatics from hydrocarbons in gasoline using two solvents DEG (diethylene glycol) and sulfolane. They used a RDC with several theoretical stages at 212 °F. The utilities required for the sulfolane process were shown to be considerably lower than for DEG, mostly because of the lower solvent flow rate required, and the lower heat capacity of sulfolane compared to DEG. They reported the total capital cost using sulfolane as 75% of that needed using DEG. They used a solvent to feed ratio of 6.8, and extracted 99% of the aromatics. A 95% recovery of sulfolane was obtained [11]. Meindersma et al. studied the recovery of aromatics from naphtha using ionic [mebupy] BF4 in a RDC [34]. The performance of the convergent-divergent column was compared with straight columns by Bandyopadhyay et al. They reported that the efficiency of the convergent-divergent column is better [4].

Table 1 Extractive processes for BTEX recovery.

Company Process	Solvent	Operating Temperature	Contracting Equipment	Comments
Shell Process, UOP	Sulfolane	120°C	Rotating disk contactor, up to 4 m in diameter	The high selectivity and capacity of sulfolane leads to low solvent-feed ratios, and thus smaller equipment.
UOP Udex Process	Diethylene glycol Triethylene glycol Tetraethylene glycol	150°C for diethylene glycol and water	Sieve-tray extractor	Tetraethylene glycol and water mixtures are claimed to increase capacity by a factor of four and also require no antifoaming agent; the extract requires a two-step distillation to recover BTX.
Union Carbide Tetra Process	Tetraethylene glycol	100°C	Reciprocating-plate extractor	The extract leaving the primary extractor is essentially free of feed aliphatics, and no further purification is necessary; two-stage extraction uses dodecane as a displacement solvent in the second stage.
Institut Français de Petróle	Dimethyl sulfoxide (DMSO)	Ambient	Rotating-blade extractor, typically 10-12 stages	Low corrosion allows use of carbon steel equipment; solvent has a low freezing point and is nontoxic; two-stage extraction has displacement solvent in the second stage.
Lurgi Arosolvan	N-methyl-2-pyrrolidionone monoethylene glycol	60°C for NMP-glycol, 35°C for NMP-water	Vertical multistage mixter-settler, 24-30 stages up to 8 m in diameter	The quantity of mixing component required depends on the aromatics content of the feed.
SNAM Progetti Formex	N-formylomorpholine	40°C	Perforated tray extractor, FM density at 1.15 aids phase separation	Low corrosion allows use of carbon steel equipment.

2.3. Experimental Method

Figure 4 summarizes the entire aromatics extraction and purification process. A well-studied typical TAG oil, soybean oil was used as the feedstock. This oil was cracked in an autoclave using a HSZM-5 catalyst, suggested by previous students at UND [7 and 24]. After cracking, a distillation unit was used to separate the heavy hydrocarbons from the lighter ones. The distillation cut was set at 145°C. The small aqueous phase was removed from the distilled crackate using separators funnel. The next step involved extracting the BTX from the rest of the crackate distillate using sulfolane.

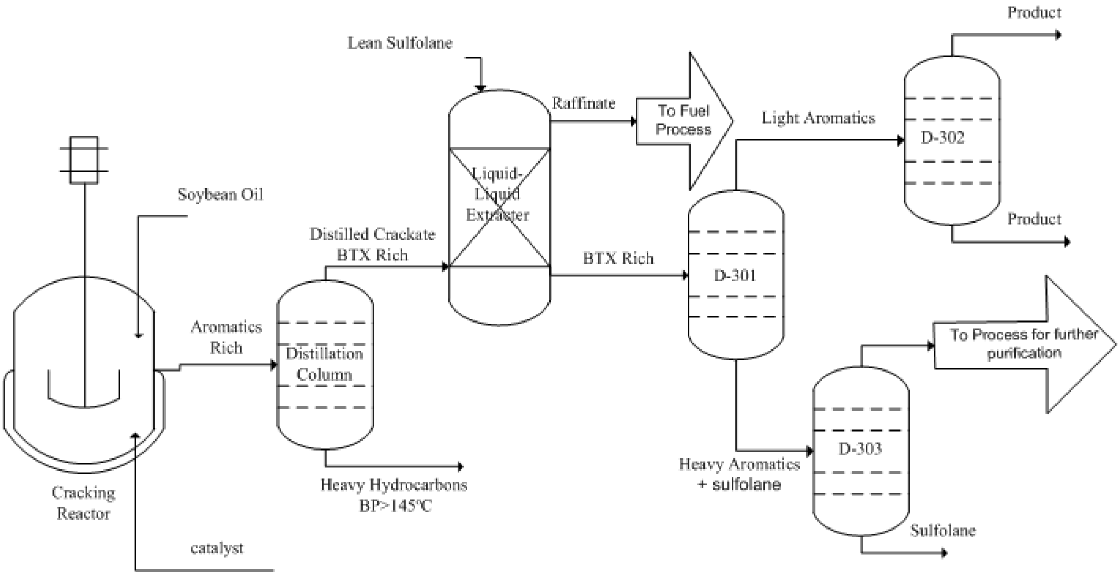

Figure 4 schematic of the whole process, generated by Microsoft Visio.

The extraction was conducted in a mixer settler bench scale set up. For Liquid Liquid Extraction (LLE), experiments were performed in three separate sets. The purification and BTX recovery was then simulated using ChemCad as discussed in chapter 3.

In this project solvent-to-solute ratio and temperature were picked as variable parameters. Sulfolane was used as the only solvent. Residence time was kept constant after a couple of screening experiments which showed the minimum time required for the mixtures to be completely mixed. The mode of operation was not tested in this project since the experiments were run in a batch mode. There was only one type of extractor used, mixer settler, due to the small scale that was picked for the experiments and simple observation. For the design criteria, the amount of mixing and settling were chosen after an initial set of screening experiments

The first set of experiments was performed using a screening design to identify the near optimum conditions for two parameters. Ratios of 3-to-1, 5-to-1, and 7-to-1 and temperatures of 30, 50 and 70 °C were tested. The rest of the parameters, initial pressure, residence time in the mixer, residence time in the settler, quantity of feedstock and type of extractor were kept constant. The ranges were chosen based on previous results [16].

A second set of experiments was then performed to determine the optimum ratio of solvent to solute to reach the maximum extraction yield that was predicted by the first set of experiments. In this set of experiments besides using of a ratio 8-to-1 and 9-to-1, the repeatability of the procedure was also checked for the ratio of 5-to-1.

A third set of experiments was needed for higher ratios. Therefore the ratio 9-to-1 was repeated and ratios of 9.5-to-1, 10-to-1, 10.5-to-1, and 11-to-1 were performed to find the optimum extraction ratio. The amount of feedstock for the ratio 10.5 and 9.5 experiments was decreased due to a lack of availability of the same feedstock for all the experiments.

2.3.1. LLE Experiment set 1

2.3.1.1. Material

Sulfolane with a 97% grade of purity was used as the solvent in these experiments. The other 3% was water which improves the extraction conditions [49]. The freezing point of sulfolane is 26°C; therefore the lowest temperature that can be used is around 30 °C, which was used as the low range value. The highest temperature was chosen to be 70 °C since the boiling point of benzene is 80.1°C at atmospheric pressure.

The solute (BTX) was assumed to be 30 % of our feedstock based on previous work [7, 24].

The feedstock was distilled cracked soybean oil (crackate). The distilled crackate from a single experiment was used for all the experiments to keep the feedstock compositions constant. Table 2 shows the average aromatics composition of distilled crackate.

Table 2 Distilled crackate aromatics composition

Compound	Weight %	Weight (g)
benzene	4%	0.18
toluene	32%	1.33
ethylbenzene	11%	0.45
o-xylene	41%	1.70
p-xylene	10%	0.40
cumene	1%	0.05
Total BTX	100%	4.12

2.3.1.2. Equipment

The LLE experiments were performed to replicate a mixer/settler arrangement. All experiments were conducted in 20 mL volume test tubes and at atmospheric pressure. A sonicator, shown in figure 5 [FS60H, Fisher Scientific]) was used as the mixer and a centrifuge [Centrific Model 228, Fisher Scientific], shown in figure 6, was used as the settler.

Figure 5 Sonicator, FS60H, Fisher Scientific

Figure 6 Centrific Model 228, Fisher Scientific

2.3.1.3. Experimental Design

The lab scale experiments were performed following a “2-Factor, 3-Level Full Factorial Experimental Design” for:

1) Ratio of the solvent to solute (3 to 1, 5 to 1 and 7 to 1)
2) Temperature of the mixer (30 °C, 50 °C and 70 °C)

For each experiment, four replicates were performed, for a total of 36 runs. Extraction yield was measured as response.

The number of experiments required to determine all the effects is given by $a^k=3^2=9$, where k is the number of the factors and a is the number of the levels.

2.3.1.4. Experimental Set Up and Procedure

The procedure for these experiments (36 total samples, six samples at a time) was as follows:

1- Using a clean beaker and pipet, add 5 g of distilled crackate to each of six test tubes.

2- Add the proper amount of sulfolane to the test tube according to table 3 for all three ratios. [For example the first set of experiments was at temperature 30 °C and replicate ratios of 3-to-1, 5-to-1 and 7-to-1, resulting in the addition of 5.1, 8.5, and 11.9 g of sulfolane, respectively].

3- Close each test tube with a cork cap and seal completely with parafilm to prevent any leakage.

4- Transfer the test tubes to the sonicator. The sonicator is operated for 10 minutes, holding six test tubes fully closed and immersed in the water basin of the sonicator. The sonicator internal heater should be used to maintain the extractor temperature at the desired level. A thermometer was used to read the temperature of the water bath. To keep record of any possible changes in the temperature of the sonicator, the temperature is recorded before and after 10 minutes. It was found to be constant during each run performed. One observation that caused some error in the results was at temperature 70 °C. At this condition, the parafilm was close to melting and some of the mixture was lost.

5- Transfer the test tubes to the centrifuge and spin for four minutes.

6- If an emulsion is observed to have formed due to over agitation, flip the tube over and the emulsion will disappear and the two phases will be distinguishable. The two phases, rich solvent (aqueous) and lean solvent (organic), should be apparent and each phase is collected and weighed, then stored for analysis.

Table 3 Weights of each stream in LLE experimental set 1

Ratio of solvent to solute	Total BTX (g)	Solvent (g)	Total distilled crackate (g)
3-to-1	1.7*	5.1	5.0
5-to-1	1.7*	8.5	5.0
7-to-1	1.7*	11.9	5.0

* 5 g of distilled crackate × 0.03+ 13% over estimation = 1.7

NB: Acetone and soapy water were used to clean the tubes. Every experiment was conducted in precisely the same way to provide consistent results.

2.3.1.5. Collection

In these lab scale experiments, the two phases are typically separated by a separating funnel, but due to the small volumes employed, disposable separating pipets were used. The two phases are rich aqueous solvent (extract) and lean organic product (raffinate). Due to the higher density of the solvent (sulfolane), the extract is heavier than the raffinate. Using a calibrated scale [accu-124D Dual Range, Fisher Scientific] an empty vial was weighed. Then the raffinate was added to the vial and it was weighed again. Whatever was left in the test tube was then poured out into a vial which was weighed before and after to determine the mass of the extract. In this part of the collection procedure there is a small loss of the raffinate phase, due to incomplete separation or as residue in the vial or pipet. To improve the mass balance, the pipet was weighed before and after use and the overall mass corrected, using this difference. Also the weight of the vial after emptying was weighed for further mass correction. The samples generated were analyzed by GC/MS to identify the aromatics compounds in each sample.

2.3.2. LLE Experiment set 2

The completion of the initial design of LLE experimental set 1 showed that a temperature of 50 °C was the optimum extraction temperature. However more experiments were needed to find the optimum solvent-to-solute ratio because the highest yield occurred at the upper DOE boundary. Therefore the only change that was made in this set of experiments was the ratio of solvent to solute. Samples with a ratio of 8-to-1 and 9-to-1, solvent-to-solute, were prepared and collected as described in section 2.3.1.

To check the repeatability, four replicates of samples with the ratio 5 to 1 at 50 °C, the middle point of the samples in LLE experimental set 1, were also performed. All the samples were prepared and collected as described in section 2.3.1.

As shown in table 4, four g of distilled crackate was used for each sample. The ratios 8-to-1 and 9-to-1 at a temperature of 50 °C were prepared according to the screening design explained above. To have valid results, four replicates were performed.

Table 4 Weights of each stream in LLE experimental set 2

Ratio of solvent to solute	total target aromatics (g)	solvent (g)	total distilled crackate (g)
8-to-1	1.2*	9.6	4.0
9-to-1	1.2*	10.8	4.0
5-to-1	1.2*	6	4.0

$*4\text{ g} \times 0.30 = 1.2\ g$

2.3.3. LLE Experiment set 3

All the procedures and equipment and material were the same as LLE experimental set 1. Table 5 shows weights used in this set of experiments. This set was used to run more ratios to better define the optimum. The ratio 9-to-1 through 11-to-1, at 0.5 increments were conducted in LLE experimental set 3. In order to use the same distilled crackate for all the ratios, the amount of distilled crackate for two of the ratios were decreased.

Table 5 Weights of each stream in LLE experimental set 3.

Ratio of solvent to solute	total target aromatics (g)	solvent (g)	total distilled crackate (g)
9-to-1	1*	9	3.3
9.5-to-1	0.36*	3.42	1.2
10-to-1	1*	10	3.3
10.5-to-1	0.36*	3.78	1.2
11-to-1	1*	11	3.3

$*3.3\ \mathrm{g} \times 0.30 = 1\ g$

$**1.2\ \mathrm{g} \times 0.30 = 0.36\ g$

2.4. Analysis of the products

2.4.1. Concentration analysis using GC

To determine the concentration of BTX on samples from each experiment, certain standards were needed. Standards and samples were prepared in the UND crop oil technologies analytical chemistry laboratory (director: Alena Kubatova) using the method and procedures found in Appendix A [59].

The analyses were performed using a high performance Gas Chromatograph coupled to parallel MS and FID detectors (SPLIT50 FID_MS_SSI_HP5_MS, figure 7). The oven was programmed as follows: 35 ℃ for 5 minutes then 30 °C/min to 300 °C for 5 minutes. A Spilt/Spiltless inlet injection method was used. The Column’s dimensions were as followed: 30 m by 250 µm by 0.25 µm [Appendix B]. Data collection and processing were performed using GC Chemstation software [24].

Figure 7 Gas Chromatograph instrument (SPLIT50_FID_MS_SSI_HP5_MS)

Standard calibration curves were plotted using the method developed previously. These standards were used to identify the concentration of target components in each sample.

2.4.2. Measurement of yield

The optimum condition was defined as the highest extraction yield of BTX. To calculate the extraction yield, one can simply divide the amount of extract by the summation of the extract and the raffinate:

Extraction yield = amount of extract (g) for total BTX/ (amount of extract (g) for total BTX + amount of raffinate (g) for total BTX)

2.5. Results and Discussion

A series of experimental runs were conducted to determine the near optimum conditions for the extraction of BTX from other hydrocarbons present in the distilled crackate of TAG oil using sulfolane. In this study the predicted variable, extraction yield, was used to determine the effects of two operating conditions.

Once all the experiments were completed, the concentration of each of the target aromatics was estimated using the calibration curves derived by standards concentration and responses from GC/MS.

2.5.1. LLE Experiment set 1 results

Assuming constant density for each compound in all experiments, the weight of the target aromatics was calculated and used to obtain the extraction yield. The extraction yields for three different ratios and temperatures are shown in Table 6. The results for this set of experiments are also shown graphically in Figure 8. It shows that the higher the solvent to solute (BTX) ratio, the higher the extraction yields. It also shows that there is no significant difference for the yield between extraction at 50 °C and 70 °C, but both temperatures gave a higher yield than extraction at 30 °C. Thus the temperature 50 °C was chosen to be near optimum for this process.

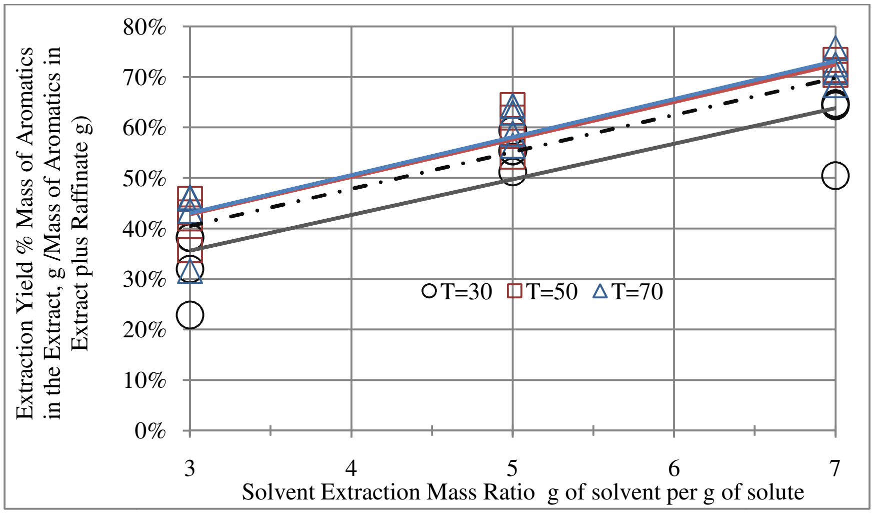

Figure 8 The extraction yield at the given temperatures and ratio

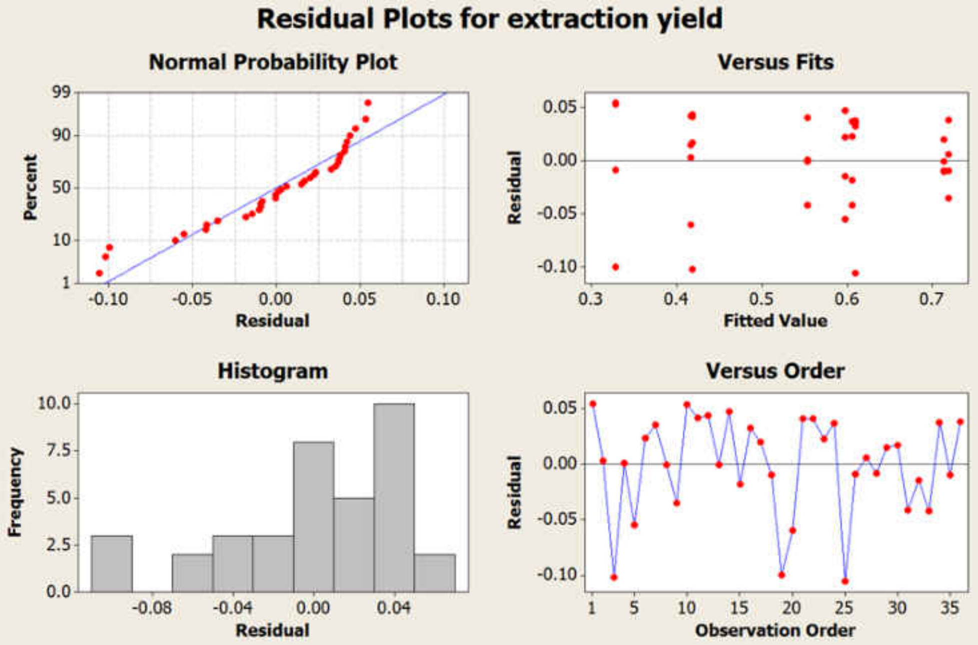

Figure 9 Normal probability plot of the residuals plotted by Minitab

Table 6 The yield extraction for the given temperatures and ratio

Actual Values		Coded Values		Response
Ratio	Temperature	Ratio	Temperature	Extraction Yield
3	30	-1	-1	38.3%
3	30	-1	-1	38.2%
3	30	-1	-1	22.9%
3	30	-1	-1	32.0%
5	30	0	-1	55.4%
5	30	0	-1	55.3%
5	30	0	-1	59.4%
5	30	0	-1	51.2%
7	30	1	-1	64.6%
7	30	1	-1	64.3%
7	30	1	-1	50.4%
7	30	1	-1	64.8%
3	50	-1	0	42.0%
3	50	-1	0	45.9%
3	50	-1	0	35.7%
3	50	-1	0	43.2%
5	50	0	0	54.2%
5	50	0	0	64.5%
5	50	0	0	62.0%
5	50	0	0	58.3%
7	**50**	**1**	**0**	**71.3%**
7	**50**	**1**	**0**	**73.4%**
7	**50**	**1**	**0**	**70.5%**
7	**50**	**1**	**0**	**70.4%**
3	70	-1	1	31.6%
3	70	-1	1	46.2%
3	70	-1	1	45.9%
3	70	-1	1	43.5%
5	70	0	1	62.9%
5	70	0	1	58.7%
5	70	0	1	64.3%
5	70	0	1	56.4%
7	**70**	**1**	**1**	**68.4%**
7	**70**	**1**	**1**	**70.9%**
7	**70**	**1**	**1**	**72.5%**
7	**70**	**1**	**1**	**75.7%**

The first assumption made in order to fit a model to data was that the errors in the data are normally distributed. Therefore the Normal probability plot of residuals was plotted using Minitab. The residual vs Fits and residual vs Order in figure 9 look like random shape. The normal probability plot of the residuals should roughly follow a straight line; however it is often difficult to tell.

To verify these observations the effect of both parameters were studied using a full factorial design (3^2) with four replicates. Statistical analyses were done using Microsoft Office Excel and the “Regression Statistics” function, displayed in table 7.

Table 7 Regression result of quadratic analysis of LLE experiment 1 complete model

Terms	Temperature^2	Ratio^2	Ratio×Temperature	Temperature	Ratio	Constant
Coefficients	-0.04	-0.05	0.005	0.04	0.15	0.61
Standard Error	0.02	0.02	0.01	0.01	0.01	0.02
R square	0.89					
F	49.35					
P-Value	0.04	0.01	0.70	2.3E-04	0.1E-15	2.6E-25
95% Error	0.04	0.04	0.02	0.02	0.02	0.04
Coefficients with Error	-0.037 ± 0.035	-0.051 ± 0.035	0.005 ± 0.025	0.042 ± 0.020	0.147 ± 0.020	0.610 ± 0.037

P-Value for term Ratio×Temperature is greater than 0.05 so this factor is not significant. Table 8 displays the revised model without Ratio×Temperature term.

Table 8 Regression result of quadratic analysis of LLE experiment 1 revised model

Terms	Temperature*Temperature	Ratio*Ratio	Temperature	Ratio	Constant
Coefficients	-0.04	-0.05	0.04	0.15	0.61
Standard Error	0.02	0.02	0.01	0.01	0.02
R square	0.89				
F	63				
P-Value	0.04	0.01	1.8E-04	1.1E-15	4.4E-26
95% Error	0.03	0.03	0.02	0.02	0.04
Coefficients with Error	-0.037 ± 0.035	-0.051 ± 0.035	0.042 ± 0.020	0.147 ± 0.020	0.610 ± 0.037

A quadratic regression was applied to find the direction for the optimum ratio to have the maximum extraction yield, by extrapolating the graph. Figure 10 shows that he projected maximum extraction yield is approximately at the higher ration that 8-to1. The regression fitted model is summarized in table 8 and equation (1). The highlighted area in figure 10 shows where the maximum extraction yield was predicted to occur.

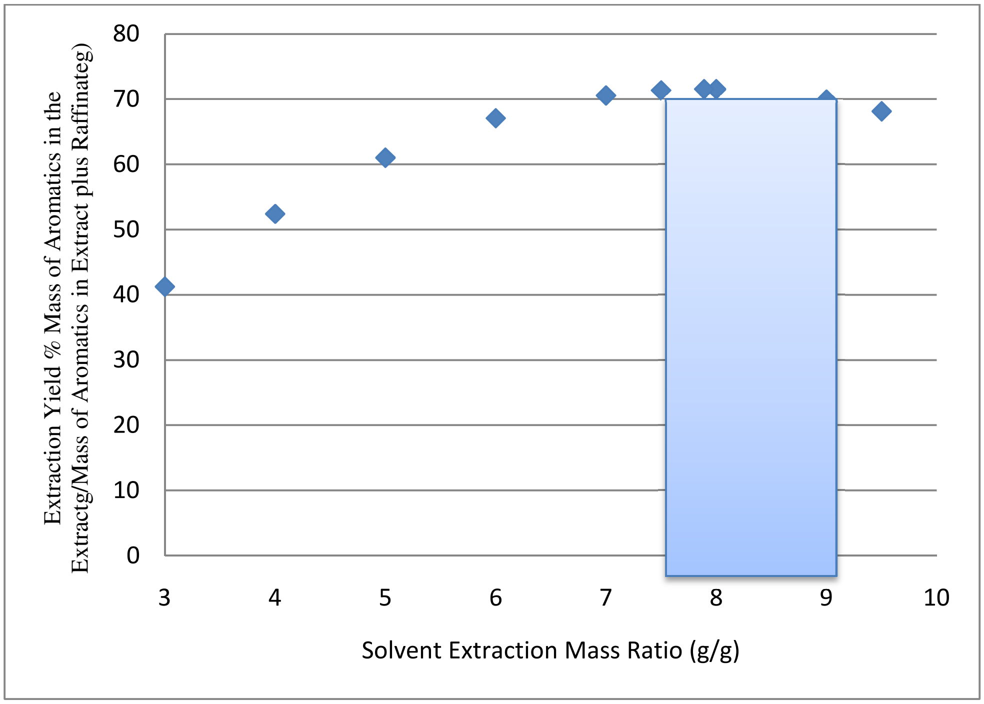

Figure 10 Extrapolation of yield vs mass ratio to estimate maximum

Equation (1):

Using equation 1 and the solver function in Excel, the highest yield was predicted to occur at ratio 8-to-1 (table 9), while figure 10 predicts ratio above 9-to-1 as the optimum. Therefore ratios 8-to-1 and 9-to-1 were performed in LLE experimental set 2 to better predict the optimum.

Table 9 Solver results to predict the maximum y with changing the Ratio

Factors	Coded Values
x_1 (Temperature)	0
x_2 (Ratio)	1.3
x_1^2 (Temperature^2)	0
x_2^2(Ratio^2)	1.6
x_1 x_2(Ratio Temperature)	0

2.5.2. LLE Experiment set 2 results

Table 10 shows the results for experiment set 2. One of the experiments at the ratio of 9-to-1 was dismissed. Due to some loss while preparing the sample for GC, the result was off.

Table 10 The yield extraction at T=50 C and three given ratios

Actual Values		Coded Values		Extract/Total
Ratio	Temperature	Ratio	Ratio* Ratio	Extraction Yield
8	50	1.5	2.25	69.5%
8	50	1.5	2.25	71.4%
8	50	1.5	2.25	50.3%
8	50	1.5	2.25	78.9%
9	**50**	**2**	**4**	**57.9%**
9	**50**	**2**	**4**	**83.7%**
9	**50**	**2**	**4**	**81.0%**
5	50	1	1	63.0%
5	50	1	1	32.1%
5	50	1	1	40.9%
5	50	1	1	47.7%

Figure 11 suggests that the higher the ratio, the higher the extraction yields, although the scatter in the data precludes being determinative in this conclusion. Additional experiments were performed in LLE experiment set 3 to resolve this uncertainty. Figure 11 also shows that the range of extraction yield for the ratio of the solvent to solute 5-to-1 from this set was within statistical accuracy of set 1 which shows that the experiments can be replicable; even then the data has a lot of scatter.

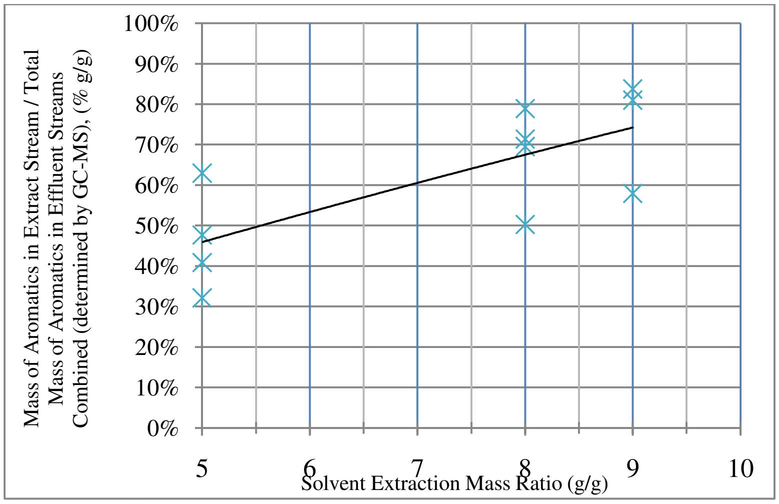

Figure 11 The extraction yield at the given temperatures and ratio

2.5.3. LLE Experiment set 3 results

Table 11 shows the results for LLE experiment set 3. The yield seems to be fairly constant from ratios of 9.5-to-1 through 11-to-1. This suggests that the maximum was reached.

Figure 12 includes the results from all the ratios in experiment set 1-to-3 for temperature 50 °C. It can be observed that the extraction yield is not significantly improving after the ratio at 9-to-1.

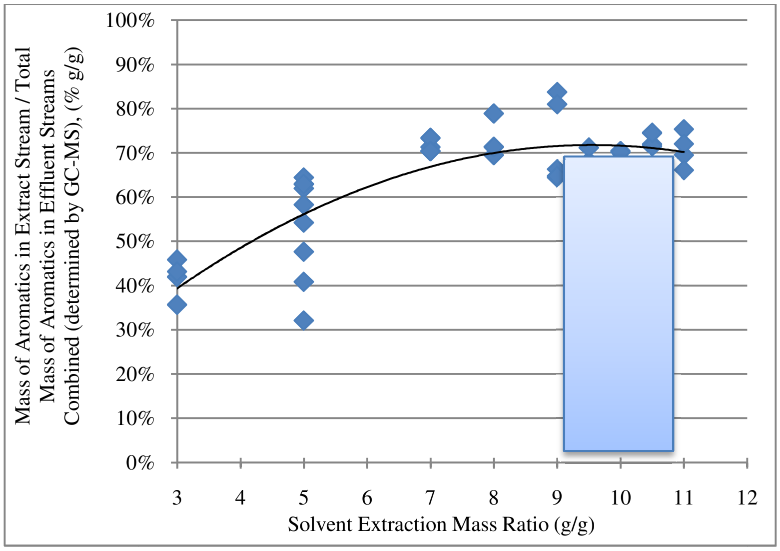

Figure 12 The extraction yield at T= 50 C for all ratios in three sets of experiments

Table 11 The yield extraction at T=50 C and five given ratios

Actual Values		Coded Values		Extract/Total
Ratio	Temperature	Ratio	Ratio* Ratio	Extraction Yield
9	50	2	4	64.5%
9	50	2	4	66.3%
9	50	2	4	55.8%
9	50	2	4	64.8%
9.5	50	2.25	5.06	68.1%
9.5	**50**	2.25	5.06	**71.2%**
9.5	50	2.25	5.06	44.1%
9.5	50	2.25	5.06	66.7%
10	**50**	2.50	6.25	**70.4%**
10	50	2.50	6.25	66.1%
10	50	2.50	6.25	68.7%
10	50	2.50	6.25	70.1%
10.5	**50**	2.75	7.56	**72.0%**
10.5	**50**	2.75	7.56	**71.5%**
10.5	50	2.75	7.56	40.5%
10.5	50	2.75	7.56	74.5%
11	50	3	9	69.5%
11	50	3	9	66.1%
11	**50**	3	9	**75.4%**
11	**50**	3	9	**72.0%**

2.6. Benzene and toluene recovery

The recovery of target aromatics for results of LLE experimental set 3 were calculated and are displayed in table 12. However the extraction yield of total compound was not significantly increasing at higher ratio than 9-to-1, but it was observed that the recovery of benzene and toluene were increasing by 10% at the ratio of 11-to-1.

Benzene Recovery = amount of benzene in the extract (g) / amount of benzene in the feed (g) * 100

Toluene Recovery = amount of toluene in the extract (g) / amount of toluene in the feed (g) * 100

Table 12 Benzene and toluene recovery

Ratio	%Benzene recovery	%Toluene recovery
9 to 1	**85%**	**71%**
	87%	**73%**
	81%	**67%**
	81%	**69%**
9.5 to 1	80%	71%
	87%	75%
	61%	50%
	81%	72%
10 to 1	88%	76%
	88%	76%
	87%	76%
	88%	76%
10.5 to 1	84%	77%
	84%	76%
	49%	41%
	74%	65%
11 to 1	**92%**	**80%**
	85%	**75%**
	91%	**81%**
	94%	**80%**

Estimation for number of stages to get a recovery of greater than 99.5% for benzene and toluene:

The results for each set of experiments are for a single stage LLE. In order to calculate the results for multiple stages LLE following assumptions were made [53]:

1- Distribution coefficient, $K_D = \frac{Y_E}{X_R}$ is constant

2- There is no sulfolane in Raffinate phase (R)

3- There is nothing but BTX + Sulfolane in extract phase (E)

- Y_E = weight of the solute in extract phase
- X_R = weight of the solute in raffinate phase

Table 13 shows the amount of benzene and toluene in extract and raffinate phase, and K_D for benzene and toluene using results from experimental set 2 for samples prepared at ratio 9-to-1.

Table 13 $\boldsymbol{Y_E, X_R,}$ ***and*** KD for benzene and toluene

	Extract		Raffinate		K_D	
Ratio	Benzene (mL)	Toluene (mL)	Benzene (mL)	Toluene (mL)	Benzene	Toluene
9 to 1	0.20	1.07	0.06	0.49	3.46	2.20
	0.21	1.09	0.05	0.46	3.84	2.40
	0.19	1.01	0.08	0.67	2.35	1.52
	0.19	1.04	0.06	0.47	3.21	2.21
	average				3.21	2.08

R= amount of hydrocarbons in raffinate phase according to table 5 = 3.3 g × (1-0.3) = 2.31 (g)

S= amount of solvent = 9 (g)

In order to find the number of stages required to have greater than 99.5% recovery of benzene and toluene, figure 13 was used [53].

E= Extraction factor = $\frac{S \times K_D}{R} = \frac{9 \times 2.08}{2.31}$=8.1

X_n/X_0=0.005

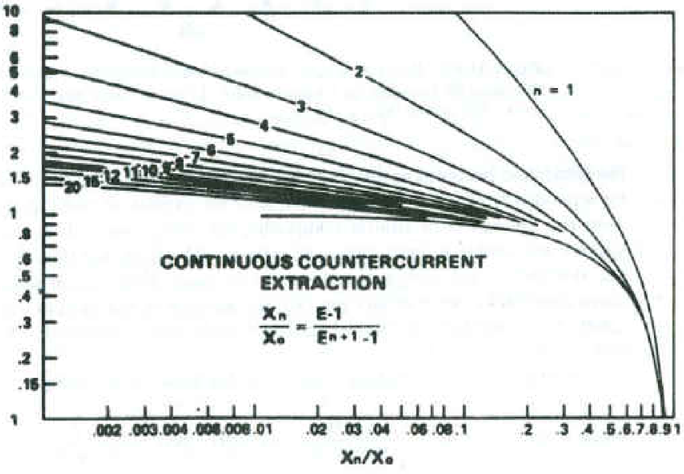

Figure 13 Relationship between unextracted solute, extraction factor, and number of stages in continues countercurrent extraction.

Therefore n= 3 was reported as the required number of stages.

2.7. Scale up LLE design and cost estimation

A column type contactor (static) with trays was designed for the LLE unit operation in this project. The amount of Distilled Crackate and solvent entering the column was simply calculated from lab scale experiments multiplies by 10 and divided by their densities at room temperature. To calculate the dimensions of the column some assumption and rules of thumbs were considered:

Velocity (m/s) = 0.01 m/s

Tray efficiency ($_{s}$) = 65 %

The number of stages was 3 according to previous section.

Calculations of diameter of column and its height:

Area 1= Volumetric flow rate of Distilled Crackate / velocity

Area 1= $\frac{4.8\ \mathrm{m^3/hr}}{36\ \mathrm{m/hr}}$ = 0.13 m^2

Area 2= Volumetric flow rate of solvent / velocity

Area 2= $\frac{8.6\ \mathrm{m^3/hr}}{36\ \mathrm{m/hr}}$ = 0.24 m^2

Area total = 0.37 m^2

Diameter of the column = $\sqrt{\frac{4*\text{Total Area}}{\pi}}$ = 0.69 m

The diameter of this column is rounded up to 1 m for standard sizing.

For this tower, with less than 1 m diameter, the actual tray separation distance is [61]:

$H_t = 0.5\ D^{0.3}$=0.5

H_a = number of stages * $\frac{H_t}{s}$ =- 2.3

For the tower the added height is 1 m [61].

The Height of this column is rounded up to 4 m for standard sizing.

The LLE was designed for a constant temperature of 50℃, therefore an internal coil was designed to be used.

The surface area of the internal coil is approximately calculated as followed [61]:

$A_{\text{internal coil}}=8\mathrm{m}^{-1}\times V_{\mathrm{LLE}}=\frac{\pi D^2}{4}\times H = 8\times\frac{\pi\times 1^2}{4}\times 4 = 8\times 3.14 = 25\ m^2$

Table 14 shows the capital cost estimation for the LLE contactor [61]. In this table the cost estimation for a heat exchanger is also added. This heat exchanger was used to preheat the feed to the distillation columns, from temperature 50 ℃ to 100 ℃, per the design discussed in section 3.3.2. Two pumps were considered to be installed, one as feed pump for the LLE and the other one as feed for the distillation section. The cost estimate is discussed in section 3.3.

Table 14 Total bare module cost for LLE in $ million

ID	Equipment Description	Capacity/Size Specification	Cp (2004)	CEPCI Jan 2004	CEPCI Feb 2012	Cp (2012)	C_{BM}	F_{BM}	Quantity	Total
LLE column	pressure vessel vertical	D 1 m, L 4 m, CS	10000	400	730.6	20092	1.5E+05	7.6	1	1.5E+05
trays	3 trays	SS	1300	400	730.6	10959	8.7E+04	2.2	3	2.6E+05
Internal coil	Surface area	25 m^2	5500	400	730.6	10046	1.7E+04	1.7	1	1.7E+04
Heater	Double pipe CS/Cu	2 m^2	1500	400	730.6	2740	1.1E+04	4.0	2	2.2E+04
pump	pump	12 hP CS	8000	400.0	730.6	14612	49680.8	3.4	2	9.9E+04
Total bare module cost										5.5E+05

3. AROMATICS PURIFICATION

3.1. Background

Distillation sometimes referred to as fractionation, is a process of separating a mixture of two or more substances into its desired purity of components based on the difference in the volatilities of the components. Distillation is the most common unit operation. It also often consumes the largest amount of energy and may contribute the most to the facilities cost.

Different types of columns can be used according to the nature of the feed that the column is processing: binary column, multi component column, multi product column, extractive distillation, azetropic distillation. The types of column internals are trayed columns and packed column.

Main components of distillation columns are as followed Figure 14:

- A vertical shell where the separation occurs
- Column internals such as tray/plate and/or packed, that are used to improve the component separation
- A reboiler that provides the vapor traffic needed for the stripping section.
- A condenser to cool and condense the vapor leaving the top of the column
- A reflux drum that holds the condensed vapor at the top of the column.
- A reflux pump to return some of the overhead liquid to the column as reflux.

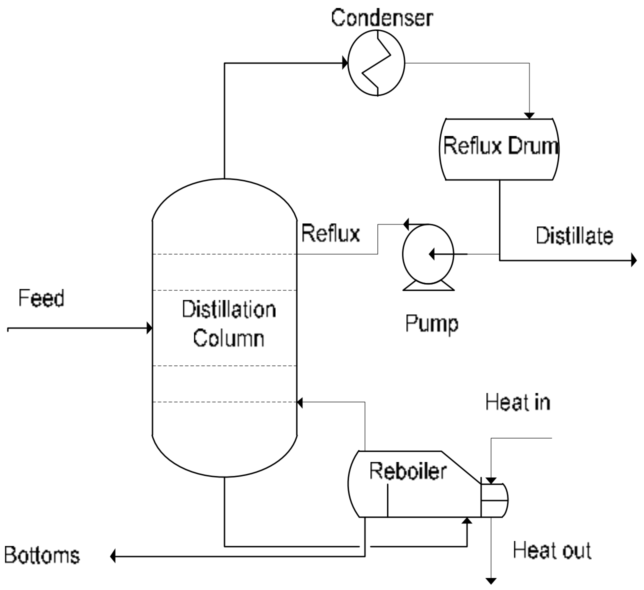

Figure 14 Main components of distillation systems

Distillation is the most common method used to purify aromatics.

3.2. Simulation modeling

Per figure 4, after extracting the aromatics by LLE, the next step is to recover the aromatics from the solvent then to purify the aromatics into commercial products. These steps can be studied efficiently and accurately using process simulation modeling. A model system was built to determine the estimated recovery of benzene and toluene and the purity of the regenerated solvent.

Different software can be used to simulate a distillation process such as: ChemCAD, Hysys, Aspen, etc. In this project ChemCAD 6.4.1 was used as the simulator. Three criteria were needed to do the simulation: an accurate composition of the feed, the accurate thermodynamic package, and the best configuration of the distillation train employed. To find the third criterion, three different configurations were modeled. Then the economics associated with each configuration was determined so that the best configuration could be selected. This is a tradeoff between the capital and operating costs.

3.2.1. Feed stream

According to analysis of the solvent from the lab-scale extraction experiments, the rich solvent stream contains the target aromatics (benzene and toluene), plus other compounds (ethylbenzene, o-xylene, p-xylene, etc.). Looking further into the GC/MS data, the presence of heavier aromatics that xylene was observed. The concentration of the target aromatics was determined analyzing the data from GC, while the rest of the compounds in the samples were not quantitatively analyzed. To have a good estimation of the amount of the other compounds, further analyses were needed such as adding those heavier aromatics, in the calibration standards which was done in LLE experimental sets 2 and 3. These compounds are heavier aromatics than the target aromatics (BTX). Some assumptions were made to estimate this quantity:

1. Aromatics heavier than xylenes were all assumed to be one compound – cumene which in previous work was found to represent most of the heavier aromatics [24].

2. It was assumed that all of the mass that entered the distillation column was the target aromatics plus cumene.

3. The entire amount of sulfolane in the LLE was assumed to be in the rich solvent stream (no sulfolane in the raffinate).

According to the results from chapter 2, the average weight of the compound in the BTX rich stream (figure 4) extract stream from LLE with the ratio of 9-to-1, is shown in table 15. These are the weight of the average samples for ratio 9-to-1 from LLE experiment set 2, multiplied by 1000. They were used in the simulation as feed for the first distillation column. Feed always entered at 100 °C and 1.01 bar.

Table 15 Average aromatics-rich solvent, extract, composition used as feed

Stream Name	Flow rates in kg/h
Water	0.0
Sulfolane	10809
Benzene	86
Toluene	494
Ethylbenzene	126
P-Xylene	125
O-Xylene	476
M-Xylene	0.0
Cumene	15

3.2.2. Thermodynamic Package

Different thermodynamic packages are used for aromatics/aliphatic mixtures and sulfolane. Among the various thermodynamic models, the non-random two-liquid model (NRTL) and the UNIversalQUAsiChemical equation (UNIQUAC) model are universal methods for estimating TAG oil compound properties. Studies show that both models can be used to correlate the experimental data [1, 21, and 50]. Lee et al. measured the VLE for a system containing sulfolane+ octane + aromatics (benzene, toluene, and p-xylene) to improve the correlation and thus the prediction of liquid-liquid equilibrium. The system was measured at 70 °C, 99 °C, and 129 °C and correlated by the UNIQUAC and NRTL models. They concluded that the NRTL fit the experimental data better [30]. Lee et al. in another study showed that for the calculated values for liquid-liquid equilibrium data for the system sulfolane + octane + benzene, sulfolane + octane + toluene and sulfolane + octane +p-xylene, the NRTL model was better than the UNIQUAC model [29].Also Ashour et al. showed that to model liquid-liquid equilibrium data for four ternary systems comprising cyclohexane + (benzene, toluene, ethyl benzene, or cumene)

+ sulfolane measured at 303.15 K and at atmospheric pressure, both UNIversalFunctionalActivityCoefficient(UNIFAC) and NRTL models represented the experimental data with sufficient accuracy [3]. Therefore NRTL was used in this study.

3.2.3. Process Model

There are a couple of different configurations for the purification of benzene and toluene from the rest of the present aromatics and sulfolane. Three different configurations were modeled in this project. For each model, an initial flash drum was used to determine the known parameters for continuous purification using three-stage distillation. Broad cost analysis was done for each configuration with some assumptions to find the best configuration for aromatics purification process.

3.2.3.1. Process Configuration 1

The first configuration is shown in figure 15. The first column separates benzene as the light key (LK) to a purity of 99.6%. The second column separates toluene as light key (LK) to a purity of 99.4%. The last column separates the sulfolane as the heavy key (HK) to 97% solvent recovery, with a mixed xylenes, ethylbenzene and cumene stream as the distillate product. Table 16 shows the parameters of the columns. Table 17 provides the stream properties of the configuration available to check the mass balance. Appendix C includes the ChemCAD reports summery for all three configurations.

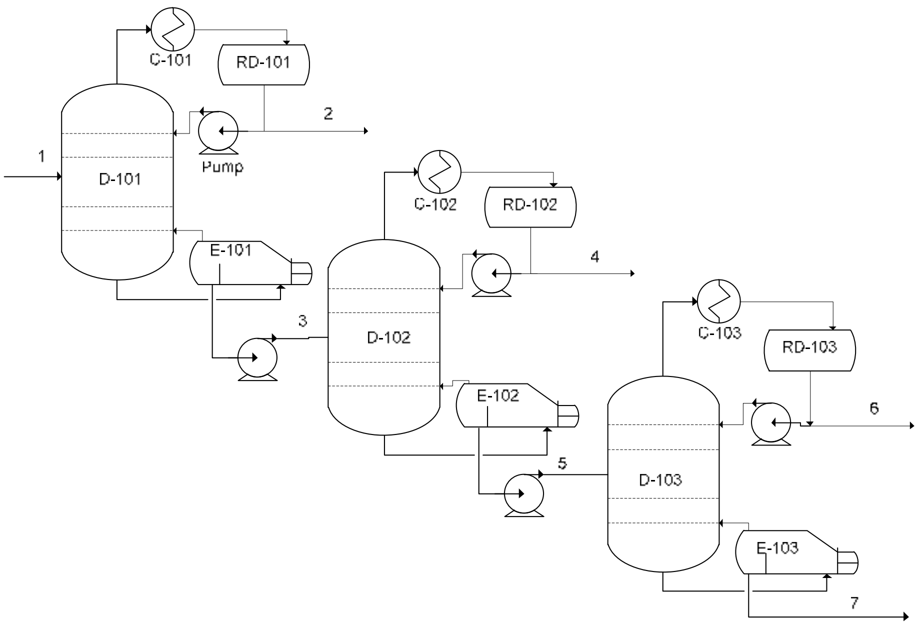

Figure 15 Process configuration 1 of three-stage distillation

Table 16 The parameters of the columns for configuration 1.

Column Number	D-101	D-102	D-103
Number of theoretical stages	21	13	7
1st feed stage	9	10	5
Calculated condenser duty MJ/h	170	1000	440
Calculated reboiler duty MJ/h	2300	2000	920
Estimated Pressure bar	1.01	1.01	1.01
Estimated. T top °C	80.1	114.3	160.7
Estimated. T bottom °C	198	244	270
Calculated Reflux ratio	3.8	5.0	1.3

Table 17 Stream parameters for configuration 1

Stream Number*	1	2	3	4	5	6	7
Temperature C	100	80.1	197.6	110.7	244	140	270
Pressure bar	1.01	1.0	1.0	1.0	1.0	1.0	1.0
Enthalpy MJ/h	-38000	63	-36000	140	-35000	-9	-35000
Vapor mole fraction	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total flow rate kg/h	12100	100	12000	500	11500	500	11000
Weight fraction							
Water	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sulfolane	89.1%	0.0%	89.7%	0.0%	93.4%	1.1%	**97.7%**
Benzene	0.7%	**99.6%**	0.0%	0.0%	0.0%	0.0%	0.0%
Toluene	4.1%	0.4%	4.1%	**99.3%**	0.2%	3.9%	0.0%
Ethylbenzene	1.0%	0.0%	1.0%	0.5%	1.1%	17.1%	0.3%
P-Xylene	1.0%	0.0%	1.0%	0.1%	1.1%	16.9%	0.4%
O-Xylene	3.9%	0.0%	4.0%	0.1%	4.1%	59.4%	1.6%
M-Xylene	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Cumene	0.1%	0.0%	0.1%	0.0%	0.1%	1.6%	0.1%

* see figure 15 for stream definitions.

3.2.3.2. Process Configuration 2

As shown in Figure 16 the first column in configuration 2 separates the sulfolane as the HK. The second column is set to separate the mixed xylenes as the HK product. Finally the last column will separate the toluene (HK) from the benzene (LK). Table 18 shows the parameters of the columns while table 19 provides the stream properties of the configuration available to check the mass balance.

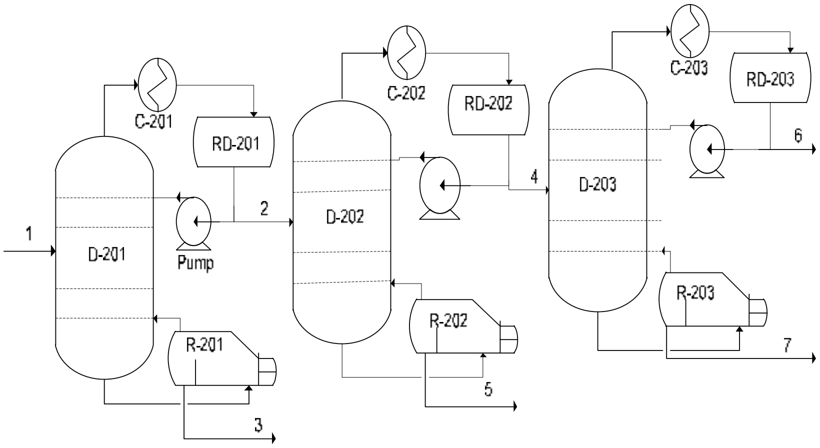

Figure 16 Process configuration 2 of three-stage distillation

Table 18 The parameters of the columns.

Column Number	D-201	D-202	D-203
Number. of stages	7	19	26
1st feed stage	2	11	14
Calculated condenser duty MJ/h	980	1100	200
Calculated reboiler duty MJ/h	4500	1150	200
Estimated Pressure bar	1.01	1.01	1.01
Estimated. T top ℃	111.0	102.6	80.1
Estimated. T bottom ℃	260.5	142.0	110.3
Calculated Reflux ratio	1.3	4.3	4.9

Table 19 Stream parameters for configuration 2

Stream Number*	1	2	3	4	5	6	7
Temperature ℃	100	113.3	265.5	102.6	142	80.1	110.3
Pressure bar	1.01	1.0	1.0	1.0	1.0	1.0	1.0
Enthalpy MJ/h	-38000	140	-35000	200	-49	61	140
Vapor mole fraction	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total flow rate kg/h	12100	1000	11100	580	420	90	490
Weight fraction							
Water	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sulfolane	89.1%	1.7%	**96.9%**	0.0%	4.0%	0.0%	0.0%
Benzene	0.7%	8.6%	0.0%	14.9%	0.0%	**99.6%**	0.4%
Toluene	4.1%	49.6%	0.0%	85.0%	0.9%	0.4%	**99.4%**
Ethylbenzene	1.0%	8.8%	0.3%	0.1%	20.8%	0.0%	0.1%
P-Xylene	1.0%	8.1%	0.4%	0.0%	19.2%	0.0%	0.0%
O-Xylene	3.9%	22.8%	2.2%	0.0%	54.3%	0.0%	0.0%
M-Xylene	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Cumene	0.1%	0.4%	0.1%	0.0%	1.0%	0.0%	0.0%

* see figure 16 for stream definitions.

3.2.3.3. Process configuration 3

In the last configuration studied (shown in Figure 17), the first column separates between a LK of toluene and HK of xylene. The next two columns are set in parallel with one, separating benzene (LK) from toluene (HK) and the other sulfolane (HK) from the mixed xylenes (LK). Table 20 shows the parameters of the columns. Table 21 provides the stream properties of the configuration available to check the mass balance.

Table 20 The parameters of the columns

Column Number	D-301	D-302	D-303
Number. of stages	11	24	10
1st feed stage	6	12	7
Calculated condenser duty MJ/h	1100	202	344
Calculated reboiler duty MJ/h	4200	206	777
Estimated Pressure bar	1.01	1.01	1.01
Estimated. T top ℃	102.2	80.0	136.7
Estimated. T bottom ℃	246.7	110.4	286.9
Calculated Reflux ratio	4.3	5.0	1.4

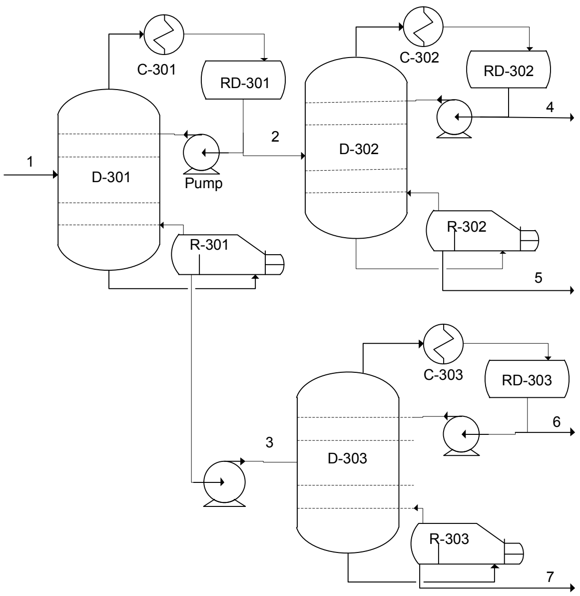

Figure 17 Process configuration 3 of three-stage distillation

Table 21 Stream parameters for configuration 3

Stream Number	1	2	3	4	5	6	7
Temperature ℃	100	102.2	241.1	80.3	110.5	137.1	269.2
Pressure bar	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Enthalpy MJ/h	-38000	190	-35000	62	130	14	-35000
Vapor mole fraction	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total flow rate kg/h	12100	600	11500	100	500	500	11000
Weight fraction							
Water	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Sulfolane	89.1%	0.01%	93.3%	0.0%	0.0%	0.0%	**96.7%**
Benzene	0.7%	15.8%	0.0%	**99.5%**	0.3%	0.0%	0.0%
Toluene	4.1%	83.9%	0.3%	0.5%	**99.3%**	8.8%	0.0%
Ethylbenzene	1.0%	0.1%	1.1%	0.0%	0.2%	17.1%	0.5%
P-Xylene	1.0%	0.1%	1.1%	0.0%	0.1%	16.5%	0.5%
O-Xylene	3.9%	0.1%	4.1%	0.0%	0.1%	56.1%	2.2%
M-Xylene	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Cumene	0.1%	0.0%	0.1%	0.0%	0.0%	1.5%	0.1%

* see figure 17 for stream definitions

3.3. Results and cost estimation

In order to find the best configuration, capital and operating costs for the main components of the distillation systems were estimated [61]. Note that pumps that are illustrated in figures 14 - 16 have not been included in the cost analysis, since it was assumed that the pressure within every column was near atmospheric, therefore the cost for pumps and the utilities needed for them were assumed to be $8E^{+03} with 12 hP energy consumption [12]. Examples are based on the properties of the first column in configuration 1:

3.3.1. Column Design (D-101)

Diameter Calculation:

$$u_{s,g} = K_{SB}\left(\frac{\rho_l - \rho_g}{\rho_g}\right)^{1/2}$$

K_{SB} = Souders-Brown constant suumed to be 0.09 m/s

ρ_l and ρ_g were the density of the liquid and vapor found at the tray with maximum volumetric flow rate.

$$u_{s,g} = 0.09\left(\frac{1006.17 - 2.77}{2.77}\right)^{1/2} = 0.09\ \mathrm{m/s}$$

$$D = \left(\frac{4VM_g}{\pi\rho_g u_{s,g}}\right)^{1/2} = \left(\frac{4 * 0.01 * 94.27}{\pi * 2.77 * 0.09}\right)^{1/2} = 2.09\ \mathrm{m}$$

V= maximum molar flow rate kgmol/s

M_g= gas molecular weight

Height calculation:

$$H_t = 0.5D^{0.3} = 0.5 * 2.5^{0.3} = 0.66\ \mathrm{m}$$

$$H_a = N\frac{H_t}{\varepsilon_s} = 21 * \frac{0.66}{0.65} = 21.26\ \mathrm{m}$$

ε_s = overall tray efficiency = 65%

The added height to H_a is 2 m.

Therefore the height of the column 1 configuration 1 is 23 m.

$$HETP = \frac{0.5D^{0.3}}{\varepsilon_s} = \frac{0.5 * 2.5^{0.3}}{0.65} = 1.01\ m$$

The material of the column is considered to be carbon steel (cs) while the tray material chosen is stainless steel (ss). Table 22 shows the diameter, height and HETP of each column for all three configurations.

Table 22 Size of columns in each configuration

configuration 1	Calculated diameter(m)	Estimated diameter (m)	H_t(m)	Column Height (m)	HETP (m)
D-101	2.09	2.50	0.66	23	1.01
D-102	1.93	2.00	0.62	14	0.95
D-103	1.22	1.50	0.56	8	0.87
configuration 2					
D-201	3.06	4.00	0.76	10	1.17
D-202	2.02	2.50	0.66	21	1.01
D-203	0.85	1.00	0.50	22	0.77
configuration 3					
D-301	2.86	3.00	0.70	14	1.07
D-302	0.86	1.00	0.50	21	0.77
D-303	1.1	1.50	0.56	11	0.87

3.3.2. Reboiler Design (R-101)

Kettle reboilers were used in all columns. According to a rule of thumb [61], the higher pressure and more corrosive liquid usually pass on the tube side. Therefore steam with 46 bar is going through the tubes. The overall heat transfer coefficient (U) was chosen from typical U values for various types of service shell and tube heat exchangers (table in reference [61]). U=700 W/m^{2}K was used for this system. The hot side fluid was water (steam) while the cold side fluid was the other process streams, assuming the composition is close to fuel oils. The material cs/Cu was used. The area of the reboiler was needed for cost estimation. The reboilers were modeled using ChemCad and the area was given by the ChemCad simulator. 46 bar steam was used in all reboilers. The steam entered at 300°C for all reboilers.

The amount of steam needed for each reboiler was also calculated by ChemCad. Table 23 shows the area and the mass flow rate of steam for each reboiler for three configurations.

Table 23 Kettle reboiler area and mass flow rate of steam for three configurations

configuration 1	heat exchanger area (m^2)	Estimated area (m^2)	Steam Temperature °C	Steam mass flow rate at 46 bar (kg/s)
R-101	10.00	10	300.00	0.42
R-102	21.94	22	300.00	0.48
R-103	25.54	26	300.00	0.15
Total				1.04
configuration 2				
R-201	97.03	98	300.00	1.52
R-202	3.77	4	300.00	0.21
R-203	0.90	1	300.00	0.06
Total				1.78
configuration 3				
R-301	24.41	25	300.00	0.85
R-302	0.88	1	300.00	0.06
R-303	91.14	92	300.00	0.73
Total				1.65

3.3.3. Condenser design (C-101)

Double pipe heat exchangers were modeled by ChemCad to calculate the area of the condensers. The inlet temperature of cooling water used in each condenser was 30°C while the outlet temperature was 45°C. The amount of cooling water for each condenser was calculated by ChemCad. $U=700\ W/m^2K$ can be used for this system according to table in Ulrich [61]; the cold side was water and hot side as hydrocarbons (light). Table 24 shows the information for condensers. CS was chosen as the material of construction.

Table 24 Condenser area and mass flow rate of cooling water.

Configuration 1	Condenser Area (m^2)	Estimated Area (m^2)	cooling water mass flow rate (m3/s)
C-101	1.91	2	0.0008
C-102	7.64	8	0.0056
C-103	1.80	2	0.0021
Total			0.0085
Configuration 2			
C-201	4.73	5	0.0046
C-202	8.03	9	0.0054
C-203	2.29	3	0.0009
Total			0.0110
Configuration 3			
C-301	7.71	8	0.0052
C-302	2.36	3	0.0010
C-303	1.59	2	0.0017
Total			0.0078

3.3.4. Reflux Drum Design (RD-101)

Horizontal decanters were sized assuming 10 minutes hold up at 50% tank volume. It is assumed that all the reflux drums are horizontal pressure vessels with minimum pressure drop across the tank. The volumetric flow rate is obtained from ChemCad.

$$\text{Volume of drum } (\mathrm{m}^3) = 2 \times \frac{\text{Volumetric flow rate}}{10 \text{ minutes} \times 60}.$$

For column 1 configuration 1 the sizing is as followed:

Volumetric flow rate = 0.40 m^3/hr

$$\text{Volume of the drum} = 2 \times \frac{0.4 \times 10}{60} = 0.13 \mathrm{~m}^3$$

$$\text{Volume} = \frac{\pi D^2}{4} \times W \rightarrow WD^2 = \text{volume} \times \frac{4}{\pi} = 0.17 \mathrm{~m}^3$$

Guess D = 0.4 m

$$\text{if } 2.5 < \frac{W}{D} < 4 \; then\ D\ is\ correct\ guess$$

$$\mathrm{W} = \frac{0.17}{0.4^2} = 1.06\ \mathrm{m}$$

Table 25 shows the final size for reflux drums for each column in all three configurations.

Table 25 Reflux drum sizing

Configuration 1	Actual Vol rate of liquid coming out of tray 1 (m^3/hr)	Reflux drum D (m)	Reflux Drum W (m)	volume of drum (m3)	W×D^2	W/D
RD-101	0.40	0.40	1.06	0.13	0.17	2.65
RD-102	3.06	0.70	2.65	1.02	1.30	3.79
RD-103	0.85	0.50	1.44	0.28	0.36	2.89
Configuration 2						
RD-201	1.65	0.60	1.95	0.55	0.70	3.24
RD-202	3.12	0.70	2.70	1.04	1.32	3.86
RD-203	0.51	0.40	1.35	0.17	0.22	3.38
Configuration 3						
RD-301	2.98	0.70	2.58	0.99	1.27	3.69
RD-302	0.52	0.40	1.38	0.17	0.22	3.45
RD-303	0.75	0.50	1.27	0.25	0.32	2.55

3.4. Description of process

3.4.1. Major Equipment List

The major equipment list for all three configurations included LLE contactor, distillation columns, condensers, reboilers, and reflux drums. In this project the bare module cost for the designed equipment was calculated. Pumps were not designed due to the assumption of the atmospheric pressure for all equipment with no pressure drop in the columns. Therefore the cost for pumps was assumed to be equal to 8000 $ for the year 2004.

3.4.2. Product List

The price for benzene and toluene were both assumed the same at a 99.9% purity at 5.47$/lb and 13.7 $/gal price in the market, respectively [70-71]. Table 26 displays the product flow rate and sale price for all three configurations.

Table 26 Products List for the Process

Configuration	Benzene kg/yr	Toluene kg/yr	Benzene $/yr	Toluene $/yr	Revenue $/year
1	7.5E+05	4.1E+06	9.01E+06	1.73E+07	2.63E+07
2	7.3E+05	4.3E+06	8.77E+06	1.79E+07	2.67E+07
3	7.4E+05	4.0E+06	8.83E+06	1.67E+07	2.55E+07

3.4.3. Raw Material List

Soybean Oil was considered as the raw material for this process. It costs 1.114 $/kg [74]. Table 27 displays the raw material, which is the same for all three configurations. Also the left over cracked oil leaving the LLE is assumed to be processed into hexane. Therefore it is assumed that the rest of the oil that is in the raffinate stream after LLE will be used to produce hexane. The price for hexane is $3.267 per gal. [73]

Table 27 Raw Material List for the Process

Component	Flow Rate (kg/hr)	Cost
Cracked Crop Oil	4000	$3.9E+07
Hexane	2678	($2.4E+07)
Net Cost		$1.52E+07

3.4.4. Utility Requirement List

Utilities required for this process include cooling water for condensers, one grade of steam for reboilers, and natural gas as the fuel used to generate each utility. Table 28 displays the utility requirements for each process configuration.

- Natural Gas:

C_{sf} = \$4.7/GJ is for 2012 [72].

- Cooling Water:

For configuration 1 cooling water is $\dot{q} = 0.01 \frac{m^3}{s}$

$cost\ for\ cooling\ water(\frac{\$}{m^3}) = (0.00007 + 2.5 \times 10^{-5} \times \dot{q}^{-1} \times CEPCI/100 + 0.003 \times C_{sf})$ = 1.1E+06 \$/yr

- 46 bar Steam:

Mass flow rate = 1.20 kg/s

Process steam price \$/yr= $(2.3 \times 10^{-5} \dot{m}_s^{-0.9} \times CEPCI/100 + 0.034 P^{0.05} \times C_{sf}) \times 24 \times 365$ =5.4E+05 \$/yr

Table 28 Utility Requirement List for all three configurations

Utility	Quantity	Cost
Natural Gas		\$4.7/GJ
Cooling Water Configuration 1	0.01 m^3/s	1.1E+06 \$/yr
46 bar Steam Configuration 1	1.20 kg/s	5.4E+05 \$/yr
Total Configuration 1		1.6E+06 \$/yr
Cooling Water Configuration 2	0.01 m^3/s	9.5E+05 \$/yr
46 bar Steam Configuration 2	1.94 kg/s	5.4E+05 \$/yr
Total Configuration 2		1.5E+06 \$/yr
Cooling Water Configuration 3	0.01 m^3/s	1.1E+06 \$/yr
46 bar Steam Configuration 3	1.81 kg/s	5.4E+05 \$/yr
Total Configuration 3		1.7E+06 \$/yr

3.4.5. Rough Planning Schedule

The total time requirement for this project is 30 months, based on the delivery time of 12 months for the process vessels. Therefore, the total capital cost is split over 30 months on the cash flow sheet. Table 29 displays the total project time.

Table 29 Rough Planning Schedule

Schedule	
Material Procurement	12 months
Implementation	9 months
Design	9 months
Total	30 months

3.5. Economic Assessment

3.5.1. Broad Cost Estimate

The broad cost was performed using the Guthrie-Ulrich method. The current Chemical Engineering Plant Cost Index (CEPCI) for equipment value was used for these cost estimates to bring costs to today's value. This value is 730.6 for February 2012 for equipment and the CE Index is 596.3. Tables in Ulrich were used to estimate the cost for all unit operations [61]. Appendix D displays the fixed capital cost for all three process configurations.

To calculate the total cost investment (TCI) the following steps were taken:

Fixed Capital (FC) which is the money that spent once and cannot be quickly converted to cash was calculated. It equals either the Grass roots costC_{GR} or C_{TM}= total module cost.

$C_{TM} = total\ module\ capital = 0.18 * C_{TBM} + C_{TBM}$ (The factor 0.18 is for contingency and fee)

This now is fixed capital needed to install a battery-limits module

For a total new plant $C_{GR} = C_{TM} * 0.3 + C_{TM}$

In this project since it is a new plan FC = C_{GR}

Typically Working capital (WC) is the value of one month's raw material inventory and two or three month's product inventory. For predesign estimate, 1- to 20 % of fixed capital is typical. 15% was used in this project.

Total Capital (TC) = FC + WC.

TC is the total amount that must be provided by investors. TC is the initial cash outflow for a project. Table 30 shows the TC and details for each configuration. The LLE cost is constant for all configurations and is added to the cost for other major units.

Table 30 Total cost investment for all three configurations

	Total bare module cost (C_{TBM})	$C_{TM} = 0.18{*}C_{TBM} + C_{TBM}$	$FC = C_{GR} = C_{TM}{*}0.3 + C_{TM}$	WC	TC=WC+FC
Configuration 1	4.30E+06	5.1E+06	6.6E+06	9.9E+05	7.6E+06
Configuration 2	5.27E+06	6.2E+06	8.1E+06	1.2E+06	9.3E+06
Configuration 3	4.16E+06	4.9E+06	6.4E+06	9.6E+05	7.3E+06

3.5.2. Manufacturing (Operating) Cost:

Table 31 displays the operating cost for all three configurations. Details of the table are explained as follows:

Table 31 Operating cost for all three process configurations in million

Configuration	Raw Material	Chemicals	Operating Labor	Maintenance	Utilities	Yearly Total
1	$15.2	$0.32	$0.37	$0.40	$1.6	$17.9
2	$15.2	$0.75	$0.37	$0.49	$1.5	$18.2
3	$15.2	$0.10	$0.37	$0.38	$1.7	$17.7

- Raw Material

Raw material comprises the highest direct manufacturing cost. From the mass balance multiply by 31.5×10^6 s/yr to convert from a second to a year basis. Table 27 shows the cost for raw material in this process.

- Chemicals

The amount of solvent that was needed to add to the LLE was different for each configuration. For example for configuration 1 table 17 shows, 1.1% of stream 6 (500 kg/hr) is the amount of sulfolane that is lost in the whole process. Therefore the price for sulfolane per year is calculated as followed:

$$0.01 \times 500\frac{kg}{hr} \times \frac{1.82\$}{lb} \times 593.6/527.9 \times \frac{2.2lb}{kg} \times 24 \times 365 = \$2.25E^{+05}/yr$$

Table 32 shows the amount and price for sulfolane for all three configurations. The price of sulfolane for October 2009 was $1.82/lb with a CE Index value of 527.9 was used to convert the price to February 2012[12]. Also according to previous works zeolite was used as catalyst in cracking reactor, shown in figure 4, with the ratio of oil-to-catalyst of 5-to-1 [7, 24]. The price for catalyst was $0.09/kg, as a rule of thumb, a 15% make up rate is assumed to be used for this process; therefore the price for catalyst is as followed [61]:

$$\frac{4000kh}{hr} \div 5 \times \frac{0.09\$}{kg} \times 0.15 \times 24 \times 365 = \$9.5E^{+04}/yr$$

Table 32 Raw Material List for the Process

Configuration	Sulfolane $/yr	Sulfolane kg/yr	zeolite $/yr	Total $/yr
1	2.3E+05	5.0E+04	9.5E+04	3.2E+05
2	6.5E+05	1.4E+05	9.5E+04	7.5E+05
3	2.1E+03	4.8E+02	9.5E+04	9.7E+04

- Operating Labor

To calculate the number of people that are needed to run the equipment the cost of labor can be estimated from the flow sheet based on the number of labors needed per major equipment. For this project the numbers of operators per unit per shift are as followed:

Process vessels

Towers (including pump and exchanger): 0.3

Separator: 0.1

Heat exchanger: 0.05

For the overall process after LLE unit, 3 towers, 1 separator and 1 heat exchanger were used, therefore:

$$0.3 \times 3 + 0.1 \times 1 + 0.05 \times 1 = 1.05\ operators\ per\ shift\ is\ needed$$

A total of 5 shifts per day for 40 hours per week are needed for a continuous process, therefore:

$$1.05\ \frac{operators}{shift} \times 5\frac{shift}{day} = 5.25\frac{operators}{whole\ unit}$$

When specific data is not available, a typical cost of $41,600 per year is assumed for chemical allied workers (2003). From 1992 to 2003, hourly wages grew at a rate of 3% per year. It was assumed that this rate stayed the same to 2020, thus the annual operator salary was calculated as followed [61]:

$$Annual\ operator\ salary = \$41{,}600 \times (1.03)^{(2012-2003)} = \frac{\$5.4E^{+04}}{year}$$

$$6\frac{operators}{whole\ unit} \times \frac{\$5.4E^{+04}}{year \times operator} = \frac{\$3.2E^{+05}}{year}$$

Operating supervision is 15% of labor cost; therefore the total labor cost is $0.37 million.

- Maintenance

According to Ulrich the maintenance and repair is 2 to 10 % of fixed capital per year. 6% of FC was used for all three configurations [61].

$Maintenance = 0.06 \times FC$

- Utilities

The utilities for this process are shown in table 28.

3.5.3. Revenue

Revenue generated by this process is based on benzene and toluene whole sale prices. Table 26 displays the price for the products in this process.

3.5.4. Taxes

Taxes are based on a 35% federal rate and 6.4% North Dakota rate. The combined tax is 39.2%. A twenty year MACRS table was used to calculate depreciation costs for each process configuration.

3.5.5. Cash Flow Sheet Calculation

For configuration 1 as an example, the calculation is as follows:

- Gross Profit, Year 1, configuration 1

  Gross profit for every year = the difference between revenues and operating cost

  $$\$26.3 million - \$17.9\ million = \$\ 8.5\ million/year$$

- Tax Basis Depreciation, year 1, configuration 1

  Tax basis depreciation is calculated by multiplying the fixed capital investment by the corresponding MACRS factor

  $$0.1 \times \$\ 6.6\ million = \$\ 0.66\ million$$

- Taxable Income, year 1, configuration 1

  Taxable income = the year's gross profit – the year's tax based depreciation

  $$\$8.46\ million - \$0.66\ million = \$\ 7.80\ million$$

- Income Tax, year 1, configuration 1

  Income tax= taxable income for the year × combined tax rate (39.2%)

$$\$7.80\ million \times 0.392 = \$3.06\ million$$

- Net Profit, year 1, configuration 1

  The yearly net profit = gross profit – income taxes

$$\$\ 8.46\ million\ - \$3.06\ million = \$5.40\ million$$

- PV@MARR, year 1, configuration 1 (MARR=12%)

  The yearly value is determined by calculating the future value of the net profit $=Future \times (1+i)^{-n}, n = year$

$$\$5.40\ million\ \times (1+0.12)^{-1} = \$\ 4.82\ million$$

- PV @ DCFROR, year 1, configuration 1

  The DCFROR value was calculated using the Microsoft excel IRR(NPV, guess=0.01) function. The PV@DCFROR was calculated the same way as PV@ 12% with the difference of using DCFROR = 49% instead of 12%.

$$\$5.40\ million\ \times (1+0.49)^{-1} = \$\ 3.6\ million$$

3.5.6. Overall Profitability

The summary of the total cost, the yearly operating cost, the present value of each configuration after twenty years, based on MARR of 12% compared to the initial cost, and the DCFROR of each configuration, is displayed in table 33. This table includes the results for ratio 9-to-1 of solvent-to-solute ratio, to compare the results. The cash flow sheet results for all three configurations are displayed in tables 34-36.

Table 33 Summary of economic assessments

Ratio	Configuration	TCI in million	Yearly operating cost in million	NPV@12% in million	DCFROR
9-to-1	1	$7.6	$17.9	$31	49%
	2	$9.3	$18.2	$30	42%
	3	$7.3	$17.7	$29	47%

Table 34 Cash flow sheet for the configuration 1 (in million)

Year	Revenue	Capital Investment	Operating Expenses	Gross Profit	Tax-Basis Depreciation	Taxable Income	Income Tax	Net Profit	PV @ 12% MARR	PV @ DCFROR
-2	$0	($1.52)	$0	$0	$0	$0.00	$0.00	($1.52)	($1.90)	($3.4)
-1	$0	($3.04)	$0	$0	$0	$0.00	$0.00	($3.04)	($3.40)	($4.5)
0	$0	($3.04)	$0	$0	$0	$0.00	$0.00	($3.04)	($3.04)	($3.0)
1	$26.3	$0	$17.9	$8.46	($0.66)	$7.80	$3.06	$5.40	$4.82	$3.6
2	$26.3	$0	$17.9	$8.46	($0.59)	$7.87	$3.08	$5.38	$4.29	$2.4
3	$26.3	$0	$17.9	$8.46	($0.53)	$7.93	$3.11	$5.35	$3.81	$1.6
4	$26.3	$0	$17.9	$8.46	($0.48)	$7.98	$3.13	$5.33	$3.39	$1.1
5	$26.3	$0	$17.9	$8.46	($0.44)	$8.02	$3.15	$5.31	$3.02	$0.7
6	$26.3	$0	$17.9	$8.46	($0.39)	$8.07	$3.16	$5.30	$2.68	$0.48
7	$26.3	$0	$17.9	$8.46	($0.35)	$8.11	$3.18	$5.28	$2.39	$0.32
8	$26.3	$0	$17.9	$8.46	($0.32)	$8.14	$3.19	$5.27	$2.13	$0.22
9	$26.3	$0	$17.9	$8.46	($0.28)	$8.18	$3.21	$5.26	$1.90	$0.15
10	$26.3	$0	$17.9	$8.46	($0.26)	$8.20	$3.22	$5.24	$1.69	$0.10
11	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$1.50	$0.07
12	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$1.34	$0.04
13	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$1.20	$0.03
14	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$1.07	$0.020
15	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$0.96	$0.013
16	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$0.85	$0.009
17	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$0.76	$0.006
18	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$0.68	$0.004
19	$26.3	$0	$17.9	$8.46	($0.23)	$8.23	$3.23	$5.23	$0.61	$0.003
20	$26.3	$0.99	$17.9	$9.45	($0.23)	$9.22	$3.61	$5.84	$0.61	$0.002
								NPV =	$31	
								DCFROR =	49%	

Table 35 Cash flow sheet for the configuration 2 (in million)

Year	Revenue	Capital Investment	Operating Expenses	Gross Profit	Tax-Basis Depreciation	Taxable Income	Income Tax	Net Profit	PV @ 12% MARR	PV @ DCFROR
-2	$0	($1.86)	$0	$0	$0	$0.00	$0.00	($1.86)	($2.33)	($3.8)
-1	$0	($3.72)	$0	$0	$0	$0.00	$0.00	($3.72)	($4.17)	($5.3)
0	$0	($3.72)	$0	$0	$0	$0.00	$0.00	($3.72)	($3.72)	($3.7)
1	$26.7	$0	$18.2	$8.44	($0.81)	$7.63	$2.99	$5.45	$4.87	$3.8
2	$26.7	$0	$18.2	$8.44	($0.73)	$7.72	$3.02	$5.42	$4.32	$2.7
3	$26.7	$0	$18.2	$8.44	($0.65)	$7.79	$3.05	$5.39	$3.84	$1.9
4	$26.7	$0	$18.2	$8.44	($0.59)	$7.85	$3.08	$5.36	$3.41	$1.3
5	$26.7	$0	$18.2	$8.44	($0.53)	$7.91	$3.10	$5.34	$3.03	$0.92
6	$26.7	$0	$18.2	$8.44	($0.48)	$7.97	$3.12	$5.32	$2.70	$0.64
7	$26.7	$0	$18.2	$8.44	($0.43)	$8.01	$3.14	$5.30	$2.40	$0.45
8	$26.7	$0	$18.2	$8.44	($0.39)	$8.06	$3.16	$5.29	$2.13	$0.32
9	$26.7	$0	$18.2	$8.44	($0.35)	$8.10	$3.17	$5.27	$1.90	$0.22
10	$26.7	$0	$18.2	$8.44	($0.32)	$8.13	$3.19	$5.26	$1.69	$0.16
11	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$1.51	$0.11
12	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$1.35	$0.077
13	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$1.20	$0.054
14	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$1.07	$0.038
15	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$0.96	$0.027
16	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$0.86	$0.019
17	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$0.76	$0.013
18	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$0.68	$0.009
19	$26.7	$0	$18.2	$8.44	($0.28)	$8.16	$3.20	$5.24	$0.61	$0.007
20	$26.7	$1.21	$18.2	$9.66	($0.28)	$9.37	$3.67	$5.98	$0.62	$0.005
								NPV =	$30	
								DCFROR =	42%	

Table 36 Cash flow sheet for the configuration 3 (in million)

Year	Revenue	Capital Investment	Operating Expenses	Gross Profit	Tax-Basis Depreciation	Taxable Income	Income Tax	Net Profit	PV @ 12% MARR	PV @ DCFROR
-2	$0	($1.47)	$0	$0	$0	$0.00	$0.00	($1.47)	($1.84)	($3.2)
-1	$0	($2.93)	$0	$0	$0	$0.00	$0.00	($2.93)	($3.28)	($4.3)
0	$0	($2.93)	$0	$0	$0	$0.00	$0.00	($2.93)	($2.93)	($2.9)
1	$25.5	$0	$17.7	$7.81	($0.64)	$7.17	$2.81	$5.00	$4.46	$3.4
2	$25.5	$0	$17.7	$7.81	($0.59)	$7.21	$2.83	$4.98	$3.97	$2.3
3	$25.5	$0	$17.7	$7.81	($0.53)	$7.27	$2.85	$4.96	$3.53	$1.5
4	$25.5	$0	$17.7	$7.81	($0.48)	$7.33	$2.87	$4.94	$3.14	$1.0
5	$25.5	$0	$17.7	$7.81	($0.44)	$7.37	$2.89	$4.92	$2.79	$0.71
6	$25.5	$0	$17.7	$7.81	($0.39)	$7.42	$2.91	$4.90	$2.48	$0.48
7	$25.5	$0	$17.7	$7.81	($0.35)	$7.46	$2.92	$4.88	$2.21	$0.32
8	$25.5	$0	$17.7	$7.81	($0.32)	$7.49	$2.94	$4.87	$1.97	$0.22
9	$25.5	$0	$17.7	$7.81	($0.28)	$7.52	$2.95	$4.86	$1.75	$0.15
10	$25.5	$0	$17.7	$7.81	($0.26)	$7.55	$2.96	$4.85	$1.56	$0.10
11	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$1.39	$0.07
12	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$1.24	$0.046
13	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$1.11	$0.031
14	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$0.99	$0.021
15	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$0.88	$0.014
16	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$0.79	$0.010
17	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$0.70	$0.007
18	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$0.63	$0.004
19	$25.5	$0	$17.7	$7.81	($0.23)	$7.58	$2.97	$4.84	$0.56	$0.003
20	$25.5	$0.96	$17.7	$8.76	($0.23)	$8.53	$3.35	$5.42	$0.56	$0.002
								NPV =	$29	
								DCFROR =	47%	

4. CONCLUSIONS

This study identified the range of near-optimum aromatics extraction conditions using sulfolane. For a single stage set up, the optimum extraction yield was found to be around 70%, while the ratio of the solvent to solute (BTX) was around 9-to-1. It was shown that using 3 stages for the same conditions the recovery of benzene and toluene will go up to 99.5%. The optimal temperature was found to be 50℃.

The ratio of sulfolane-to-distilled crackate for the optimum extraction yield was 2.7-to-1 which is close to what is used for UOP process. Therefore with the number of stages 3 and Temperature 50 ℃ and the ratio of solvent-to-solute 2.7-to-1, it can be concluded that the results are comparable to UOP results.

Simulations demonstrated that BTX products of commercial purity, greater than 99%, can be generated using traditional distillation technology. According to a cost analysis, three configurations have similar net profit value over 20 years. Besides the higher NPV for configuration 1, comparison of reboilers duty shows that this configuration is easier to build, therefore configuration 1 is recommended as the best configuration for this process. Table 37 displays the summary of cost analysis of all three configurations.

Table 37 Summary of cost analysis for all three configuration.in million

configuration	Revenue	NPV@12%	DCFROR	TCI
1	$26	**$31**	49%	$7.6
2	$27	$30	42%	$9.3
3	$26	$29	47%	$7.3

Although, configuration 1 has slightly higher NPV@12% than the other two, the results are statistically inconclusive. Therefore more detailed cost analysis is needed for all three configurations to make a valid conclusion.

5. RECOMMENDATIONS

In this project for the LLE process, single stage extraction was used. It was shown that with 3 stage extraction the greater yield can be obtained. It is recommended to run the experiments for 3-stage LLE to confirm the estimated number of stages.

Although the results are comparable to UOP results, a more detailed economic analysis is needed to determine the best purification configuration.

Extractive distillation methods have been widely used to separate components with close boiling point while using certain solvents to raise their relative volatility. It is recommended to model this method as well.

In distillation modeling, for non-ideal mixtures, the program can only make estimates by using thermodynamic equations such as UNIFAC. For more precise results experimental data is recommended to be used.

More detailed cost analysis is recommended for all three configurations in order to make a statically valid conclusion.

APPENDICIES

APPENDIX A. Concentration analysis method and procedures

Standard preparation for the calibration curves:

Following the procedure below:

Preparing the Stock Solution

1- Weigh the empty vial

2- Add 90 µL of benzene and weigh

3- Add 90 µL of toluene and weigh

4- Add 90 µL of ethyl benzene and weigh

5- Add 90 µL of o-xylene and weigh

6- Add 90 µL of p-xylene and weigh

7- Add 1350 µL of MeOH and weigh

8- Cap and weigh the vial

The concentration of each compound in each standard is known. Using the responses of the standards, the calibration curves were plotted. These calibration curves were used to identify the concentration of each compound in the samples.

In any calibration and sample analysis an Internal Standard (IS) is necessary. The reason is that even though the auto sampler works well there is no perfect injection. Therefore an IS was prepared for these sets of samples as follows: In a 22 mL vial 0.2 mL of 2-chlorotoluene was added using a pipet. Then 20 mL of MeOH was added as solvent.

Standards for calibration were prepared in 2 mL auto sampler vials as followed:

1. First step was to prepare the stock solution:
    a. Weigh an empty 40 mL vial
    b. Add 6 mL of MeOH and weigh
    c. Add 500 µL of cumene and weigh
    d. Add 500 µL of p-xylene and weigh
    e. Add 500 µL of o-xylene and weigh
    f. Add 500 µL of ethylbenzene and weigh
    g. Add 500 µL of toluene and weigh
    h. Add 500 µL of benzene and weigh
    i. Total 9 mL of stock solution is ready

NB: at the end of adding all compounds to have full mixing flip the capped vial 3 times.

2. To prepare the standard number 1 (STD1), 0.9 mL of stock solution was added to the empty vial, then 0.9 mL MeOH was added to the vial
3. To prepare the STD2, 0.9 mL of STD1 was added to the empty vial, the 0.9 mL MeOH was added to the vial
4. To prepare the STD3, 0.9 mL of STD2 was added to the empty vial, the 0.9 mL MeOH was added to the vial
5. To prepare the STD4, 0.9 mL of STD3 was added to the empty vial, the 0.9 mL MeOH was added to the vial
6. To prepare the STD5, 0.9 mL of STD4 was added to the empty vial, the 0.9 mL MeOH was added to the vial

7. To prepare the STD6, 0.9 mL of STD5 was added to the empty vial, the 0.9 mL MeOH was added to the vial
8. To prepare the STD7, 0.9 mL of STD6 was added to the empty vial, the 0.9 mL MeOH was added to the vial
9. To prepare the STD8, 0.9 mL of STD8 was added to the empty vial, the 0.9 mL MeOH was added to the vial
10. To prepare the STD10, 0.9 mL of STD9 was added to the empty vial, the 0.9 mL MeOH was added to the vial, then 0.9 mL of the mixture in the vial ws dumped.
11. To each vial 100 µL of IS was added and then they all were capped.

Sample preparation:

1. Weigh an empty 2 mL auto sampler vial
2. Add .01 mL of sample
3. Weigh the vial to keep record of the density of each sample
4. Add .08 mL of MeOH
5. Add 0.1 mL of IS
6. Cap the vial

APPENDIX B. Gas chromatography settings full description

```
INSTRUMENT CONTROL PARAMETERS:    7890 GC-FID-TCD-MSD
-----------------------------------------------------

   D:\METHODS\ASHWINI\12-0208_SPLIT50_FID_MS_SSI_HP5-MS_Btex_NK.M
      Wed Feb 08 15:55:00 2012

Control Information
------- -----------

Sample Inlet      :  GC
Injection Source  :  GC ALS
Mass Spectrometer :  Enabled

Oven
Oven                                 On
Equilibration Time                  0.5 min
Oven Program
    35 degrees C for 5 min
    then 30 ºC/min to 300 degrees C for 5 min

Post Run Temperature                 35 degrees C

Front Injector

Front Inlet PTV
Heater                              Off
Pressure                            Off
Total Flow                          Off
Septum Purge Flow                   Off
Mode                             Splitless
Gas Saver                           Off
Temperature Program
    250 degrees C for 0 min
Vent Flow                             0 mL/min
Vent Pressure                         0 Until 0
Injection Pulse Pressure              0 Until 0
Cryo                                Off

Back Inlet SS
Heater                               On    300 ░C
Pressure                             On    15.863 psi
Total Flow                           On    59.1000000041347 mL/min
Septum Purge Flow                    On    3 mL/min
Mode                              Split
Gas Saver                            On    20 mL/min After 2 min
```

```
Split Ratio                          50 :1
Split Flow                           50 mL/min
Injection Pulse Pressure         689475 Until 0.75

Front Aux Heater
Heater                               On
Temperature Program
    300 degrees C for 0 min

Column #1
J&W 19091S-436: 350 ºC: 60 m x 250 ╡m x 0.25 ╡m
HP-5MS EERC : 1814.57698
In: Back SS Inlet He
Out: Aux Pressure 3

Column #2
450 ºC: 25 m x 320 ╡m x 0 ╡m

Column #3
450 ºC: 25 m x 320 ╡m x 0 ╡m

Column #4
450 ºC: 25 m x 320 ╡m x 0 ╡m

Column #5
450 ºC: 25 m x 320 ╡m x 0 ╡m

Column #6
450 ºC: 0.5 m x 320 ╡m x 0 ╡m

Front Detector FID
Heater                               On    340 ºC
H2 Flow                              On    30 mL/min
Air Flow                             On    400 mL/min
Makeup Flow                          On    25 mL/min
Const Col + Makeup                  Off
Flame                                On
Electrometer                         On

Back Detector TCD
Heater                              Off
Reference Flow                      Off
Makeup Flow                         Off
Const Col + Makeup                  Off
Negative Polarity                   Off
Filament                            Off

Valve 1

Valve 2

Valve 3
```

```
Valve 4

Valve 5

Valve 6

Valve 7

Valve 8

Signals
Front Signal                     Save On
Test Plot                        Save Off
Test Plot                        Save Off
Test Plot                        Save Off

                                MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File                : atune.u
Acquistion Mode          : Scan


MS Information
-- -----------

Solvent Delay            : 0.00 min

EM Absolute              : False
EM Offset                : 0
Resulting EM Voltage     : 1388.2

[Scan Parameters]

Low Mass                 : 50.0
High Mass                : 550.0
Threshold                : 150
Sample #                 : 2       A/D Samples    4
Plot 2 low mass          : 50.0
Plot 2 high mass         : 550.0

[MSZones]

MS Source                : 230 C   maximum 250 C
MS Quad                  : 150 C   maximum 200 C

Timed Events
----- ------

[Timed MS Detector Table Entries]

Time (min)          State (MS On/Off)
```

```
1.62                     Off
1.90                     On
9.86                     Off
10.20                    On

                             END OF MS ACQUISITION PARAMETERS

                              TUNE PARAMETERS for SN: US10739010
                        -----------------------------

 Trace Ion Detection is OFF.

 EMISSION    :      34.610
 ENERGY      :      69.922
 REPELLER    :      26.940
 IONFOCUS    :      90.157
 ENTRANCE_LE :      28.500
 EMVOLTS     :    1388.235
 AMUGAIN     :    1423.000
 AMUOFFSET   :     121.813
 FILAMENT    :       2.000
 DCPOLARITY  :       0.000
 ENTLENSOFFS :      18.573
 MASSGAIN    :    -976.000
 MASSOFFSET  :     -38.000

                           END OF TUNE PARAMETERS
                      ------------------------------------
```

APPENDIX C. ChemCAD output summary

CHEMCAD 6.4.1

Simulation name: Configuration 1 Date: 7/23/2012 Time: 13:08:13

Unit type : TOWER Equipment ID: D-101

			* Net Flows *				
Number of Stage	Temperature ºC	Pressure bar	Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h	Duties MJ/h
1	80.1	1.01	4.2			1.11	-163.4
2	80.2	1.01	4.19	5.3			
3	80.4	1.01	4.18	5.3			
4	80.9	1.01	4.16	5.29			
5	81.8	1.01	4.13	5.27			
6	83.3	1.01	4.08	5.24			
7	85.8	1.01	4	5.18			
8	90.1	1.01	3.38	5.1			
9	126	1.01	124.75	4.48	103.38		
10	130.7	1.01	127.44	22.48			
11	135.7	1.01	130.54	25.17			
12	139.1	1.01	132.85	28.26			
13	141	1.01	134.1	30.58			
14	141.8	1.01	134.67	31.83			
15	142.1	1.01	134.91	32.39			
16	142.3	1.01	135.02	32.63			
17	142.4	1.01	135.07	32.74			
18	142.8	1.01	135.11	32.79			
19	144.4	1.01	134.97	32.83			
20	152	1.01	132.18	32.69			
21	197.6	1.01		29.91		102.28	2315

Mole Reflux ratio 3.797

Total liquid entering stage: 9 at 99.738 ºC, 106.76 kmol/h.

Unit type : TOWER   Equipment ID: D-102

			* Net Flows *				
Number of Stage	Temperature ºC	Pressure bar	Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h	Duties MJ/h
1	110.7	1.01	25.86			5.17	-1036
2	110.8	1.01	25.83	31.03			
3	111	1.01	25.78	31			
4	111.4	1.01	25.68	30.95			
5	112.2	1.01	25.49	30.85			
6	113.6	1.01	25.18	30.66			
7	115.9	1.01	24.75	30.36			
8	119.3	1.01	23.99	29.92			
9	125.5	1.01	17.4	29.16			
10	183.5	1.01	115.1	22.57	102.28		
11	190.4	1.01	117.73	17.99			
12	204.9	1.01	119.74	20.63			
13	244	1.01		22.64		97.1	2025

Mole Reflux ratio 5

Total liquid entering stage 10 at 179.829 ºC, 113.257 kmol/h.

Unit type : TOWER   Equipment ID: D-103

			* Net Flows *				
Number of Stage	Temperature ºC	Pressure bar	Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h	Duties MJ/h
1	140	1.01	6.18			4.77	-439.4
2	160	1.01	3.39	10.95			
3	220.6	1.01	2.93	8.16			
4	243	1.01	3.04	7.7			
5	246.4	1.01	100.89	7.81	97.1		
6	253.5	1.01	102.87	8.56			
7	270	1.01		10.53		92.34	915

Mole Reflux ratio 1.296

Total liquid entering stage 5 at 243.934 ºC, 100.144 kmol/h.

Simulation name: Configuration 2 Date: 7/23/2012 Time: 13:44:15

Unit type : TOWER Equipment ID: D-201

* Net Flows *

Number of Stage	Temperature ºC	Pressure bar	Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h	Duties MJ/h
1	80.1	1.01	5.29			1.08	-196.3
2	80.2	1.01	5.28	6.37			
3	80.5	1.01	5.27	6.36			
4	81	1.01	5.25	6.35			
5	81.9	1.01	5.2	6.32			
6	83.7	1.01	5.13	6.28			
7	86.5	1.01	5.05	6.21			
8	90.3	1.01	4.96	6.12			
9	94.4	1.01	4.9	6.04			
10	97.8	1.01	4.87	5.98			
11	100.3	1.01	4.85	5.94			
12	101.8	1.01	4.85	5.93			
13	102.7	1.01	4.85	5.92			
14	103.1	1.01	11.27	5.92	6.43		
15	103.7	1.01	11.27	5.92			
16	104.4	1.01	11.27	5.92			
17	105.2	1.01	11.28	5.92			
18	106	1.01	11.28	5.93			
19	106.8	1.01	11.29	5.93			
20	107.6	1.01	11.3	5.94			
21	108.3	1.01	11.31	5.95			
22	108.9	1.01	11.32	5.96			
23	109.4	1.01	11.32	5.97			
24	109.7	1.01	11.33	5.98			
25	110.1	1.01	11.34	5.99			
26	110.3	1.01		5.99		5.35	200.1

Mole Reflux ratio 4.911

Total liquid entering stage 14 at 102.606 ºC, 11.271 kmol/h.

Unit type : TOWER Equipment ID: D-202

* Net Flows *

Number of Stage	Temperature ºC	Pressure bar	Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h	Duties MJ/h
1	113.3	1.01	13.51			10.35	-982.7
2	155.3	1.01	150.17	23.86	103.38		
3	166.4	1.01	156.76	57.13			
4	172.8	1.01	158.52	63.73			
5	182	1.01	152.83	65.48			
6	214.4	1.01	150.74	59.79			
7	265.5	1.01		57.7		93.03	4500

Mole Reflux ratio 1.306

Total liquid entering stage 2 at 101.473 ºC, 116.892 kmol/h.

Unit type : TOWER Equipment ID: D-203

* Net Flows *

Number of Stage	Temperature ºC	Pressure bar	Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h	Duties MJ/h
1	102.6	1.01	27.44			6.43	-1138
2	106.8	1.01	27.48	33.86			
3	108.6	1.01	27.52	33.9			
4	109.3	1.01	27.52	33.94			
5	109.7	1.01	27.5	33.95			
6	110	1.01	27.44	33.93			
7	110.4	1.01	27.34	33.87			
8	111.2	1.01	27.15	33.76			
9	112.5	1.01	26.84	33.57			
10	114.6	1.01	26.39	33.27			
11	117.9	1.01	36.42	32.82	10.35		
12	121.9	1.01	36.01	32.5			
13	126.4	1.01	35.68	32.09			
14	130.8	1.01	35.52	31.76			
15	134.5	1.01	35.49	31.6			
16	137.1	1.01	35.49	31.56			
17	138.8	1.01	35.49	31.57			
18	140	1.01	35.3	31.57			
19	142	1.01		31.38		3.92	1150

Mole Reflux ratio 4.271

Total liquid entering stage 11 at 114.216 ºC, 36.73 kmol/h.

Simulation name: Configuration 3 Date: 7/23/2012 Time: 13:56:08

Unit type : TOWER Equipment ID: D-301

* Net Flows *

Number of Stage	Temperature ºC	Pressure bar	Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h
1	102.2	1.01	26.28			6.07
2	106.6	1.01	26.29	32.35		
3	108.7	1.01	26.3	32.36		
4	109.7	1.01	26.22	32.37		
5	110.7	1.01	23.17	32.29		
6	134.6	1.01	151.12	29.24	103.38	
7	138.3	1.01	152.05	53.81		
8	145.1	1.01	153.79	54.73		
9	156.4	1.01	154.55	56.48		
10	180.5	1.01	149.08	57.24		
11	241.1	1.01		51.77		97.31
Mole Reflux ratio	4.331					
Total liquid entering stage	6 at		101.828	C	126.548	kmol/h.

Unit type : TOWER Equipment ID: D-303

* Net Flows *

Number of Stage	Temperature ºC	Pressure bar	Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h
1	137.1	1.01	5.42			3.96
2	139.7	1.01	5.41	9.38		
3	141	1.01	4.83	9.37		
4	154.1	1.01	2.72	8.79		
5	210.6	1.01	2.13	6.68		
6	237.7	1.01	2.19	6.09		
7	242.1	1.01	100.01	6.15	97.31	
8	243.6	1.01	100.51	6.65		
9	248.4	1.01	101.78	7.15		
10	264.2	1.01		8.43		93.35

Mole Reflux ratio 1.37

Total liquid entering stage 7 at 241.076 ºC, 99.503 kmol/h.

Unit type : TOWER Equipment ID: D-302

Number of Stage	Temperature ºC	Pressure bar	* Net Flows * Liquid kmol/h	Vapor kmol/h	Feeds kmol/h	Product kmol/h
1	80.1	1.01	5.46			1.09
2	80.3	1.01	5.45	6.54		
3	80.5	1.01	5.43	6.54		
4	81.1	1.01	5.4	6.52		
5	82.3	1.01	5.36	6.49		
6	84.3	1.01	5.28	6.44		
7	87.5	1.01	5.18	6.36		
8	91.4	1.01	5.1	6.27		
9	95.4	1.01	5.04	6.19		
10	98.7	1.01	5.01	6.13		
11	100.9	1.01	5	6.1		
12	102.3	1.01	11.07	6.09	6.07	
13	103.1	1.01	11.07	6.09		
14	104	1.01	11.07	6.09		
15	105	1.01	11.07	6.09		
16	106	1.01	11.08	6.09		
17	106.9	1.01	11.09	6.1		
18	107.8	1.01	11.1	6.11		
19	108.5	1.01	11.11	6.12		
20	109.1	1.01	11.12	6.13		
21	109.6	1.01	11.12	6.13		
22	109.9	1.01	11.13	6.14		
23	110.2	1.01	11.13	6.15		
24	110.4	1.01		6.15		4.98
Mole Reflux ratio	5.027					

Total liquid entering stage 12 at 101.619 ºC, 11.072 kmol/h.

APPENDIX D. Bare module cost tables

Bare module cost for all three process configurations tables 38-40.

Table 38 Total bare module cost for the process configuration 1 in $

Equipment ID	Equipment Description	Capacity/Size Specification	Cp (2004)	CEPCI Jan 2004	CEPCI Feb 2012	Cp (2012)	C_{BM}	Quantity	Total
D-101	Benzene, Toluene Separation from Xylene, Sulfolane	23 m H, 2.5 m D, cs	400	730.6	1.80E+05	1.40E+06	7.6	1	1.40E+06
Trays	21	SS	400	730.6	6.80E+03	1.60E+04	2.2	21	3.30E+05
RD-101	Reflux Drum	1 m W, 0.5 m D, cs	400	730.6	3.10E+03	1.90E+04	6	1	1.90E+04
C-101	double pipe	area 2 m^2	400	730.6	3.70E+03	1.30E+04	3.5	2	2.60E+04
R-101	Kettle reboiler cs/Cu	area 10 m^2	400	730.6	1.30E+04	5.10E+04	4	2	1.00E+05
D-102	Solvent regeneration	12 m H, 2 m D, cs	400	730.6	7.30E+04	5.60E+05	7.6	1	5.60E+05
Trays	13.00	SS	400	730.6	4.60E+03	1.20E+04	2.2	13	1.60E+05
RD-102	Reflux Drum	2.5 m W, 1 m D, cs	400	730.6	9.10E+03	5.50E+04	6	1	5.50E+04
C-102	Double pipe	area 8 m^2	400	730.6	9.10E+03	3.20E+04	3.5	2	6.40E+04
R-102	Kettle reboiler cs/Cu	area 22 m^2	400	730.6	2.00E+04	8.00E+04	4	2	1.60E+05
D-103	Benzene and Toluene Separation	7 m H, 1.5 m D, cs	400	730.6	4.60E+04	3.50E+05	7.6	1	3.50E+05
Trays	7	SS	400	730.6	2.70E+03	9.60E+03	2.2	7	6.80E+04
RD-103	Reflux Drum	1.5 m W, 0.5 m D, cs	400	730.6	3.10E+03	1.90E+04	6	1	1.90E+04
C-103	Double pipe cs/Cu	area 2 m^2	400	730.6	3.70E+03	1.30E+04	3.5	2	2.60E+04
R-103	Kettle reboiler cs/Cu	area 26 m^2	400	730.6	2.40E+04	9.50E+04	4	2	1.90E+05
pumps	pump	12 hP cs	400	730.6	1.50E+04	5.00E+04	3.4	5	2.50E+05
Total bare module cost									3.8E+06

Table 39 Total bare module cost for the process configuration 2 in $

Equipment ID	Equipment Description	Capacity/Size Specification	Cp (2004)	CEPCI Jan 2004	CEPCI Feb 2012	Cp (2012)	C_{BM}	F_{BM}	Quantity	Total BMC
D-201	BTEX Separation from Sulfolane	10 m H, 4 m D, cs	7.00E+04	400	730.6	1.30E+05	9.70E+05	7.6	1	9.70E+05
Trays	7	SS	1.00E+04	400	730.6	1.80E+04	6.40E+04	2.2	7	4.50E+05
RD-201	Reflux Drum	1.5 m W, 1 m D, cs	4.00E+03	400	730.6	7.30E+03	4.40E+04	6	1	4.40E+04
C-201	double pipe cs/Cu	area 5 m^2	4.00E+03	400	730.6	7.30E+03	2.60E+04	3.5	2	5.10E+04
R-201	Kettle reboiler cs/Cu	area 98 m^2	2.50E+04	400	730.6	4.60E+04	1.80E+05	4	2	3.70E+05
D-202	BT Separation from EX	21 m H, 2.5 m D, cs	9.00E+04	400	730.6	1.60E+05	1.20E+06	7.6	1	1.20E+06
Trays	19	SS	3.70E+03	400	730.6	6.80E+03	1.80E+04	2.2	19	3.40E+05
RD-202	Reflux Drum	3 m W, 1 m D, cs	5.00E+03	400	730.6	9.10E+03	5.50E+04	6	1	5.50E+04
C-202	double pipe cs/Cu	area 9 m2	5.30E+03	400	730.6	9.70E+03	3.40E+04	3.5	2	6.80E+04
R-202	Kettle reboiler cs/Cu	area 4 m^2	6.00E+03	400	730.6	1.10E+04	4.40E+04	4	2	8.80E+04
D-203	Benzene and Toluene Separation	22 m H, 1 m D, cs	5.00E+04	400	730.6	9.10E+04	6.90E+05	7.6	1	6.90E+05
Trays	26	SS	6.00E+02	400	730.6	1.10E+03	2.50E+03	2.2	26	6.60E+04
RD-203	Reflux Drum	1.5 m W, 0.5 m D, cs	1.70E+03	400	730.6	3.10E+03	1.90E+04	6	1	1.90E+04
C-203	double pipe cs/Cu	area 3 m^2	3.00E+03	400	730.6	5.50E+03	1.90E+04	3.5	2	3.80E+04
R203	Kettle reboiler cs/Cu	area 1 m^2	5.00E+03	400	730.6	9.10E+03	3.70E+04	4	2	7.30E+04
pumps	pump	12 hP cs	8.00E+03	400	730.6	1.50E+04	5.00E+04	3.4	3	1.50E+05
Total bare module cost										4.70E+06

Table 40 Total bare module cost for the process configuration 3 in $

Equipment ID	Equipment Description	Capacity/Size Specification	Cp (2004)	CEPCI Jan 2004	CEPCI Feb 2012	Cp (2012)	C_{BM}	F_{BM}	Quantity	Total BMC
D-301	Benzene, Toluene Separation	14 m H, 3 m D, cs	7.00E+04	400	730.6	1.30E+05	9.70E+05	7.6	1	9.70E+05
Trays	11	SS	5.50E+03	400	730.6	1.00E+04	2.70E+04	2.2	11	2.90E+05
RD-301	Reflux Drum	3 m W, 1 m D, cs	5.00E+03	400	730.6	9.10E+03	5.50E+04	6	1	5.50E+04
C-301	double pipe cs/Cu	area 8 m2	5.00E+03	400	730.6	9.10E+03	3.20E+04	3.5	2	6.40E+04
R-301	Kettle reboiler	area 25 m2	1.30E+04	400	730.6	2.40E+04	9.50E+04	4	2	1.90E+05
D-302	Solvent regeneration	9 m H, 1.5 m D, cs	3.20E+04	400	730.6	5.80E+04	4.40E+05	7.6	1	4.40E+05
Trays	10	SS	1.50E+03	400	730.6	2.70E+03	7.20E+03	2.2	10	7.20E+04
RD-302	Reflux Drum	2 m W, 0.5 m D, cs	1.70E+03	400	730.6	3.10E+03	1.90E+04	6	1	1.90E+04
C-302	double pipe cs/Cu	area 2 m2	2.60E+03	400	730.6	4.70E+03	1.70E+04	3.5	2	3.30E+04
R-302	Kettle reboiler	area 80 m2	2.50E+04	400	730.6	4.60E+04	1.80E+05	4	2	3.70E+05
D-303	Benzene and Toluene Separation	17 m H, 1 m D, cs	5.00E+04	400	730.6	9.10E+04	6.90E+05	7.6	1	6.90E+05
Trays	24	SS	6.00E+02	400	730.6	1.10E+03	2.50E+03	2.2	24	6.10E+04
RD-303	Reflux Drum	1.5 m W, 0.5 m D, cs	1.70E+03	400	730.6	3.10E+03	1.90E+04	6	1	1.90E+04
C-303	double pipe cs/Cu	area 3 m2	3.00E+03	400	730.6	5.50E+03	1.90E+04	3.5	2	3.80E+04
R-303	Kettle reboiler	area 1 m2	6.00E+03	400	730.6	1.10E+04	4.40E+04	4	2	8.80E+04
pumps	pump	12 hP cs	8.00E+03	400	730.6	1.50E+04	5.00E+04	3.4	4	2.00E+05
Total bare module cost										3.60E+06

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