IJCPS Science International Journal of Chemical and Petroleum Sciences
ISSN 2253-0932

ASPEN HYSYS SIMULATION AND COMPARISON BETWEEN ORGANIC SOLVENTS (SULFOLANE AND DMSO) USED FOR BENZENE EXTRACTION

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ABSTRACT

Due to the high increase of the production of aromatic hydrocarbons: benzene, toluene and xylenes BTX from oil because of the large activity of their big markets especially with the availability of great quantities of these aromatic fractions in the oil. This study has two main parts the first presents a general vision of the aromatic hydrocarbons, the second is going to focus on the liquid-liquid extraction with the selected solvents as a separation method. The solvent selection depends on many properties. In this second part there will be a simulation (conception and execution) of the liquid-liquid extraction of aromatics by two different organic solvents Sulfolane and DMSO followed by a comparison between the results obtained by the simulation. The simulator used will be ASPEN HYSYS 7.2.

The results of the simulation showed that the use DMSO is better than Sulfolane because of the separation efficiency the economic value and the regeneration rate although its use is more dangerous (more toxic) than the Sulfolane

Keywords: *Extraction, Aromatic, DMSO, Sulfolane, Simulation, HYSYS.*

1. INTRODUCTION

The petroleum industry has implemented several methods for separating aromatic either cutting lubricant or light petroleum cuts, among these methods there is liquid-liquid extraction. The liquid-liquid extraction is a separation technique that takes advantage of the deference solubility of components of a homogeneous liquid load in a suitable solvent [1, 4].

The addition to the load of a partially miscible solvent causes the appearance of a second liquid phase which selectively transfers to the most soluble components. Phase separation followed by decanting the solvent contained therein gives two functions whose compositions depend on the parameters of the extraction [3,10].

It uses solvent extraction when distillation alone cannot provide a good separation and good economic solution.

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In order to have a good extraction, it is necessary to use solvent contains the following features:
- Solvent power.
- Selectivity. (Solubility, selectivity, density, viscosity, temperature, it should not be expensive, toxic, corrosive, unstable ... etc...)[11].

2. OVERVIEW OF AROMATIC HYDROCARBONS

2.1 Chemical structure

Aromatic are different than other hydrocarbons by the fact that they have an aromatic cycles. And C/H ratio is high.

Benzene has the formula C_6H_6, H are all identical since the substitution of one of the six hydrogen is a radical provided by a single compound. The molecule must therefore be symmetrical. The first formula of benzene by Kekule was proposed [1]:

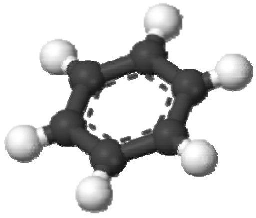

Fig.1. Benzene formula.

It makes much of the fact that all hydrogen's are identical, and there is not a single derivative substituted with a group (Y)

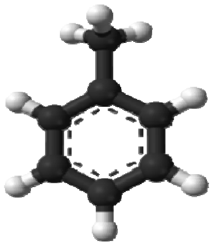

Fig.2. Toluene formula.

For Xylene three isomers could exist

- Ortho Xylene
- Meta Xylene
- Para Xylene

Table.1. Characteristics of aromatic compounds [2]

	formula	MW	Boiling Point (°C)	Melting Point (°C)	density (g/ml)	Solubility in water (g/100g)	Dielectric Constant 3,4	flash point (°C)
benzene	C6H6	78.11	80.1	5.5	0.879	0.18	2.28	-11
Toluene	C7H8	92.14	110.6	-93	0.867	0.05	2.38(25)	4
o-xylene	C8H10	106.17	144	-25.2	0.897	Insoluble	2.57	32
m-xylene	C8H10	106.17	139.1	-47.8	0.868	Insoluble	2.37	27
p-xylene	C8H10	106.17	138.4	13.3	0.861	Insoluble	2.27	27

2.2 Different methods of separation of aromatic

We can use several techniques to extract high purity aromatics species produced either in the steam cracking, or catalytic reforming.

These treatments are mostly based on physico-chemical processes and are sometimes Sir most specific economic, certain types of load or certain operating conditions although they are, in principle, able to handle all aromatic types' essences. They are: Crystallization, adsorption, distillation, azeotropic distillation, extractive distillation and solvent extraction [5, 7].

3. EXTRACTION BYSOLVENT

Liquid-liquid extraction (also called solvent extraction) was initially utilized in the petroleum industry beginning in the 1930's. It has since been utilized in numerous applications including petroleum, hydrometallurgical, pharmaceutical, and nuclear industries. Liquid-liquid extraction describes a method for separating components of a solution by utilizing an unequal distribution of the components between two immiscible liquid phases. In most cases, this process is carried out by intimately mixing the two immiscible phases, allowing for the selective transfer of solute(s) from one phase to the other, then allowing the two phases to separate[8,9].

Typically, one phase will be an aqueous solution, usually containing the components to be separated, and the other phase will be an organic solvent, which has a high affinity for some specific components of the solution.

The process is reversible by contacting the solvent loaded with solute(s) with another immiscible phase that has a higher affinity for the solute than the organic phase. The transfer of solute from one phase into the solvent phase is referred to as extraction and the transfer of the solute from the solvent back to the second (aqueous) phase is referred to as back-extraction or stripping [4].

The two immiscible fluids must be capable of rapidly separating after being mixed together, and this is primarily a function of the difference in densities between the two phases. [3, 6]

3.1 Different types of common solvents

The solvents used in industrial processes are either oxygenated sulfur compounds such as tetra ethylene sulfone (sulfolane) or dimethyl derivative. They obviously have the general properties of industrial solvents [7].

Sulfolane

diméthyle sulfoxide

Fig.3. Sulfolane and DMSO structures.

3.2 Physico-chemical properties

Table.2.*Physico-chemical properties of common solvents.*

Solvent	M(g/mol)	T_f(°C)	T_b(°C)	$\rho \frac{Kg}{m^3}$ 20 (°C)	$\frac{\mu\ (mPa.s)}{\theta\ (°C)}$	Pressure of steam (kPa)
Sulfolane	120.2	27.6	287	1266	10.3/30	1.3310^{-3}à 30°C
DMSO	78.13	18.5	190.85	1100	1.99/25	0.084 à 25°C

4. ENVIRONMENTAL PROPERTIES

4.1 Toxicological information

Table.3.*Toxicological information of common solvents.*

Solvent	Toxicityague LD_{50}		Risk indication	Values	carcinogenesis
	(Oral)	(skin)			
Sulfolane	1941	4009	R22	0.37	Negative results
DMSO	28000	50000	R36, 37,38	50	Negative results

- R36/37/38: Irritating to eyes, respiratory system and skin.
- R22: Harmful if swallowed.

4.2 Ecological information

The organic solvents mentioned are all volatile organic compounds (VOCs).Their vaporization in the atmosphere contributes to the production of ozone in the troposphere by photo chemical reaction, thus increasing the risks, especially for asthmatics or people with breathing difficulties.

The rejection of these solvents directly into the environment can contribute significantly to the deterioration of the flora and fauna inhabiting the rivers and streams.

5. THE SIMULATION STEPS

5.1 General methodology

This part is to simulate an aromatics extraction process by ordinary solvents previously presented on an industrial scale by using simulation software well known in the engineering field as ASPEN HYSYS 7.2.

5.2 Choosing a-separation system

The benzene extraction of benzene / heptane mixture by ordinary solvents was chosen as a model for aromatic / aliphatic separation.

5.3 Choice of a thermodynamic model

Data interaction parameters for the system heptane + benzene + solvent were estimated by choosing the thermodynamic model NRTL (Non Random Two Liquid), because it is the most suitable model for the simulation of liquid-liquid extraction processes.

5.4 The operating conditions

The average conditions of ordinary solvents studied in the extractor are determined according to existing industrial processes.

Table.4.*Operatingconditions of the extraction processes of aromatic industrial scale.*

Process	Solventused	Operating Conditions	Report solvent/feedstock	Number of stages
Sulfolane (Shell-Uop)	Sulfolane	100°C 2bar	4/1	12
IFP	DMSO	35°C 1bar	4/1	12

Table.5.*Data of the extraction by organic solvents process.*

	Feed		Solvent	
	Shell-UOP	IFP	Shell-UOP	IFP
Temperature °C	100	35	100	35
Pressure bar	1.013	1.013	1.013	1.013
Total flow total t/h	300	300	1600	1600
Benzene t/h	120	120	-	-
Heptane t/h	180	180	-	-
Solvent t/h	-	-	1600	1600
Composition by weight%				
Benzene	40	40	-	-
Heptane	60	60	-	-
Solvent	-	-	100	100

6. PROCESS DESCRIPTION

The feed mixture is fed to the liquid-liquid extraction tower (T-100), where aromatic hydrocarbons selectively dissolved with the solvent. The raffinate phase rich non-aromatic hydrocarbons out the top of the column and sent to the tower (T-102) for the purpose of recovering the small amount of solvent introduced into the raffinate phase. The water-solvent mixture passed to the stripper for separation. Aliphatic out the top of the splitter and sent to storage. The solvent-rich extract phase exits the extraction tower with traces of aliphatic and aromatic high quantity, they are sent to the stripper (101-T) to ensure good separation solvent / aromatic solvent leaves the pure stripper (T-101) at the bottom and recycled to the extraction tower and aromatics lot with high purity as distillate.

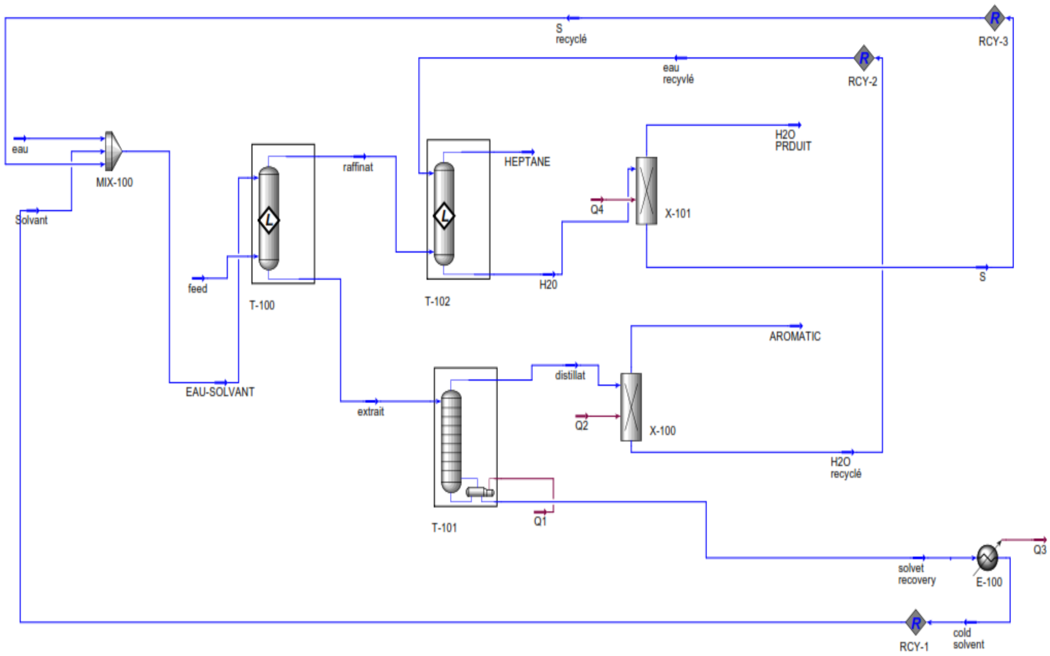

Fig.4. Technological scheme of aromatic extraction by organic solvent designed by AspenHysys7.2.

Table.6.*Results of the different processes studied.*

	Alimentation		Solvent		Bottoms		Extracted Product	
processes	1	2	1	2	1	2	1	2
Temperature °C	100	35	100	33.36	129	36.16	98	-5.89
Pressurebar	1.013	1.103	1.103	1	3	1	3	1
Total flowt/h	300	300	1206	1520	1412	1737	93.45	82.94
Benzenet/h	180	180	7.71	-	253.86	162.08	2.93	-
Heptanet/h	120	120	-	-	36.13	26.35	86.23	82.31
Solventt/h	-	-	1186.22	1289.67	1050.52	1013.86	4.19	0.60
H2O	-	-	12.06	230.32	71.49	234.70	0.08	0.02
Composition by weight %								
Benzene	60	60	0.93	-	17.98	9.33	3.14	0
Heptane	40	40	-	-	2.56	1.52	92.28	99.24
Solvent	-	-	92.77	84.85	74.4	75.64	4.49	0.73
H2O	-	-	6.29	15.15	5.06	13.51	0.09	0.03
Recovery rate %								
Benzene	-	-	-	-	0.01	-	-	-
Heptane	-	-	-	-	-	-	-	-
Solvent	-	-	-	-	98.96	99.82	100	100
H2O	-	-	-	-	0.04	0.18	-	-

. 1- Extraction by sulfolane 2- Extraction by DMSO

7. RESULTS AND COMPARISON

Following the processes carried out and which were designed to compare the rate of solvent recovery without reducing the performance of processes it has been found that there is a difference between these two.

On sulfolane, it was found that the extract contains 253 .86 t\h Benzene, while DMSO contains only 162 .08 t\h (91.78 t\h more). The amount of benzene lost in the raffinate is negligible (<3 t\h).

Pure benzene recovered was 184.19 t\h after extraction by sulfolane and 185.31 t\h by the DMSO.

Heptane for the amount in the extract was 36.1 t\h for sulfolane extraction and 26.35t\h for DMSO (difference 9.78 t\h) the major amount of heptane was in the raffinate as in sulfolane extraction processes the amount of heptane was 86.23t\h and 82.31 for DMSO (3.92 t\h difference).

The pure heptane to recover the end of the process is: 85.38 t \ h after extraction sulfolane and 113.2 t \ h after extraction by DMSO.

According to that introduced 300 t\h mixing (180 t\h benzene and 120 t\h heptane) in the extraction column was recovered 269.57 t\h in sulfolane extraction (89.85%) and 298.51t\h by the method of DMSO (99.50%).

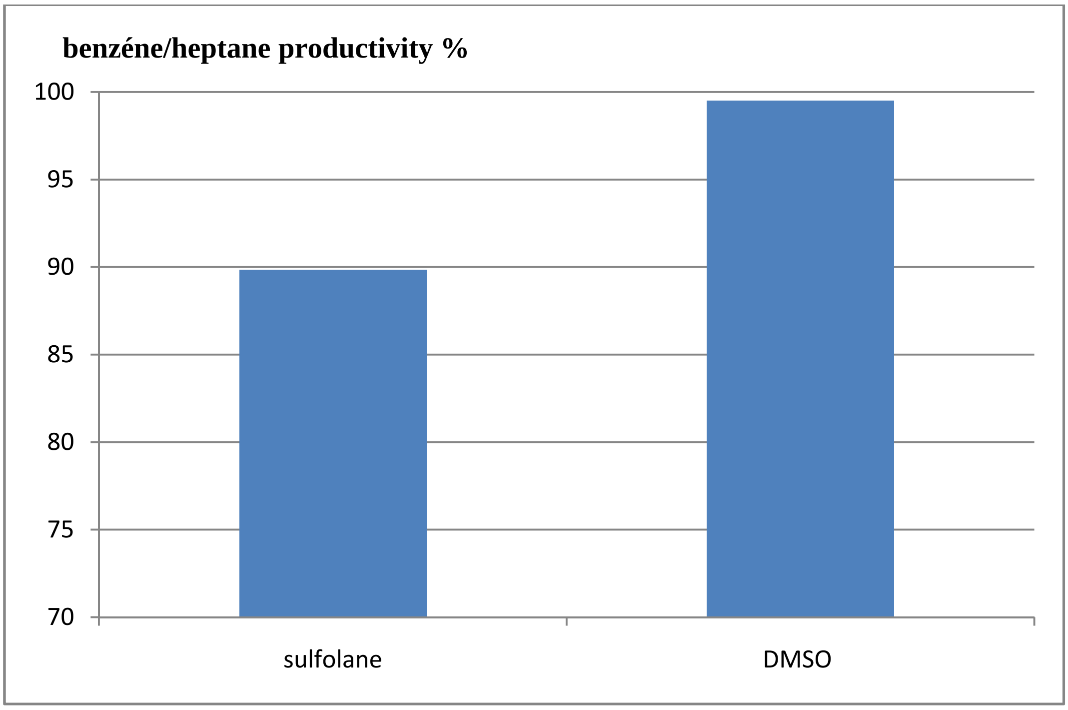

Fig.5. Products obtained at the end of the process.

7.1 The solvents

a- Regeneration rate

Sulfolane introduced into the extraction column is 1186.22 t\his recovered solvent is 1179.84t\h (99.31% sulfolane was recovered).
DMSO introduced into the extraction column is 1289.67 t\h and recovered DMSO is 1185.12 t\h (99.90% solvent was recovered).

b- Economic comparison

Proposed by the company of Liaoyang Guanghua Chemical Co.., Ltd. Standard sulfolane price in the market is 3700 $ per ton. In the process we will use 1206 ton of sulfolane that reach up to 4,462,200 $.
99.31% of sulfolane was recovered means that there is a lost value of 30,789.18$ per hour.

The reasonable price of DMSO is about 2100$ for ton (2.1$ / kg) so as proposed by Hansen Zhuzhou Chemical Co., Ltd. 1520 ton will be used with the value of 3,192,000$.

99.90% DMSO was recovered means that the lost value of this solvent is 3.192$ per hour.

While DMSO is cheaper than sulfolane as the total difference is 1,270,200$ and the difference of the lost (per hour) is 27,597.18$.

8. CONCLUSION

We have seen in this work the importance of separation processes and took the liquid-liquid extraction as a separation method in industry and its economic importance.
For benzene in the aromatic hydrocarbons, liquid-liquid extraction is probably the best method of separation and the solvents used are generally organic.
The preparation and the choice of solvent is probably the main processes such as extraction is chosen such as to form with the support a mixture of two immiscible phases and must not only allow the separation of the products but also be easily used in extractors and easily separable from the dissolved products and its use should be as economical as possible.
In this work we used two organic solvent which are: tetramethylene sulfone (sulfolane) and dimethyl sulfoxide (DMSO) and compared the results of these last two in the industry by simulation (with HYSYS 7.2).
We used the thermodynamic model NRTL (Non Random Two Liquid), because it is the most suitable for the simulation of liquid-liquid extraction processes model.
The procedures were similar for both solvents means that the same equipment was used for the separation and recovery same conditions operating power but operating conditions solvents were not the same after the nature of the two different solvents.

From the results obtained it was found that DMSO was better than sulfolane for different reasons as it has better selectivity capacity miscibility regeneration rate and economic value although it is more toxic than sulfolane.

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