STUDY OF ADSORPTION DEMIXING HEAT TRANSFORMER WORKING ON PARTIALLY MISCIBLE MIXTURE

By

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CERTIFICATION OF APPROVAL

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Approved by,

_____
Dr. Rajashkhar Pendyala

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TRONOH, PERAK
August 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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Hannah Blanca Jariol Paylaga

ACKOWLEDGEMENTS

ABSTRACT

Rising problems of energy recovery and depletion are the possible danger most industries are facing now. The usage of effective equipment that does not only solve energy depletion but also environmental friendly has become a natural course for solving such bottlenecks for every industry. A heat driven technology, Adsorption Demixing Heat Transformer (ADHT) offers solutions by upgrading low temperature to high temperature by the use of waste heat or geothermal energy. To further investigate this technology, analysis of three working pairs of water-furfural, n-heptane – DMF and cyclohexane –DMSO were investigated as the driving force of ADHT. The efficiency of the three pairs of mixture on its operating parameters such as its internal temperature lift and thermal yield were demonstrated by the use of Hysys software. Projected results showed a temperature lift of 8.4, 5.7 and 36 K for water-furfural, n-heptane – DMF and cyclohexane-DMSO respectively. In conclusion, cyclohexane and DMSO pair has been found out as the best working pair with the highest temperature and thermal yield of 0.998 for better optimum results for an ADHT.

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CHAPTER 1: INTRODUCTION

1.1.0   BACKGROUND OF STUDY

Industrial companies are undergoing various problems on getting higher production process. Absorption Heat Transformer (AHT) offers a promising solution for these on the production and environment process of an Industrial plant. It also offers varieties of opportunities to the Industries' bottlenecks on improving energy efficiency and reducing primary energy consumption by the use of waste heat or geothermal energy as the heat source by upgrading or delivering heat at higher temperature. AHT is a kind of heat pumps that offers the least – cost option in troubleshooting on greater production and on the other hand which is also one of the best way on reducing combustion emissions which makes it environmentally friendly (Laborelec, 2007).

Figure 1: The use of geothermal Energy

AHT belongs to the absorption cycle or the heat driven technology pump. Different types of AHT use different mechanisms but all of which are using working pair (refrigerant – absorption solution) as the working fluid. Amongst all of the study a new trend rise on the use of Absorption Demixing Heat Transformer (ADHT) of which the research is focused about.

Figure 2: CO2 emission of Industries

ADHT is found out to offer better result of performance compared to AHT and furthermore, it is less costly and has simpler design. It works best on a different working pair compared to the common working pair (H_2O/ LiBr) used in typical AHT. It uses mixtures that are partially miscible and exhibits a miscibility gap at lower temperature. This research is based on the comparative studies of partially miscible mixtures: i) N- heptanes / N, N- dimethyl formamide (DMF), ii) water / furfural (C3H3 OC) CHO and iii) Cyclohexane / Dimethyl Sulfoxide (DMSO). The operating parameter that identifies the efficiency of the machine is determined via simulation results.

1.1.1 PROBLEM STATEMENT

The following are the problem statement:

- To review the efficiency of ADHT
- To compare and to find the best suitable mixture between partially miscible mixtures:
    - Water / Furfural
    - N- heptanes / DMF
    - Cyclohexane / DMSO

1.1.2   OBJECTIVES AND SCOPE OF STUDY

This study is based on the new type of absorption cycle and the research project should meet the following objectives:

- To determine the following operating parameters of each pair of mixtures:
  - Internal Temperature Lift (ΔT_i)
  - Thermal Yield (ηth)
- Comparison of the performances of the following partially miscible mixtures:
  - Water / Furfural
  - N- heptanes / DMF
  - Cyclohexane / DMSO

1.1.3   RELEVANCY OF THE PROJECT

The performance of an ADHT is a key significant factor for industrial use to produce useful heat at high temperature level from a low temperature level from waste heat. As most of the Industries have encountered various problems of how to reuse back the waste energy being released off in the atmosphere and the energy source depletion the understanding of how an Absorption cycle works is important. ADHT is all before AHT and the mechanisms behind this machine is put into studies in order to greatly validate the feasibility of the new cycle with its operating parameters. The project is expected to come up with a comparative result on the three (3) pairs of partially miscible mixtures being used with its operating parameters.

1.1.4   FEASIBILITY OF THE PROJECT WITHIN THE SCOPE AND TIME FRAME

Simulation values are expected at the end of this study with the operating parameters of the three (3) pairs of chemicals. Considerations on the use of Hysys simulation will take place beforehand. The collection of data and the operating parameters are gained in order to validate in the calculation through Matlab. Within the time frame given for Final Year Project II, this experiment is expected to finish at the time given.

CHAPTER 2: LITERATURE REVIEW

Depletion of energy has come to its peak. Oil which is the main source of energy has caught the mass media for its decreasing source. Researchers are on the go on digging up other replacement of source of energy with the use of a renewable energy. Machines and equipments were born back then and as century has passed by some of the Industries had faced problems on how to effectively use equipment that does not only use renewable energy but are also environmentally friendly such as the reduce emission amount of CO_2 and costless. In the world of Heat Pumps, studies and researches have proved the great work of AHT but until now it is still rarely practice because it's only able to upgrade heat from 30 to 50% of the driving waste heat to an interesting temperature level (Yin et al., 2000) and its uprising drawbacks such as corrosion problems and crystallization limits. Suggested by many from previous studies the use of an absorption cycle an ADHT that are less exergy destructive by simply replacing the distillation column of the typical AHT to a settler which makes it less expensive and the having possibility of working the entire unit without any throttling device or pump.

Table 1 shows the undertaken researches of ADHT. AHT works best with its working pair and these usually use binary mixtures. Whilst on the other hand, ADHT performs best with a different pair of mixture that has an Upper Critical Solution Temperature (UCST).

Table 1: Undertaken Research of ADHT

No	Author/Year	Undertaken researches	Working Pair	Result/s (COP, ^{o}C)
1	Niang et al , 1997	Experimental	Water/ Furfural	0.86
2	Alonso et al, 2002	Experimental	N-heptane/DMF	Calculation= 0.93; Experiment = 0.40
3	Alonso et al, 2003	Simulation	Cyclohexane/ DMSO & N-heptane/DMF	0.96
4	Noubli et al, 2011	Simulation	N-heptane/DMF	5.9

2.1.0 WORKING PAIRS

Chemicals or substances that are mixed together are used for AHT. With the use of these working pairs it can produce or induce heat energy without altering the composition mechanically or chemically which is then useful for cooling and heating (Wongsuwan, 2001).

Working fluids with the combination of LiBr/ H_2O is the most common working pairs studied by most researchers (Rivera et al., 2000, Ma et al., 2003, and Saravanan 2011). Others used NaOH/ H_2O (Stephan et al., 1997), H2O – LiBr + Lil + LiNo3 + LiCl (Bourouis et al., 2004), Water/ Carrol^{TM} Mixture (W. Rivera et al., 1999),etc.

Combination of working fluids should both have an excellent refrigerant and good absorbent and which Gutierrez suggested that the absorbent should have higher affinity for the refrigerant. Below are the required properties (Spinner et al., 1993) on finding such working pairs:

- Low viscosity
- Low surface tension
- High thermal conductivity
- High external heat transfer coefficient
- Non – toxic
- High latent heat
- High affinity High storage capacity
- Small specific volume
- Non - corrosive
- Economic criteria
- Cost and Performance Criteria
- Thermal stability

2.1.1 CLASSICAL AHT

AHT is composed of five main components which are evaporator, generator, heat exchanger, absorber and condenser. It works when there is a lower energy amount (Q_{eva}) at the evaporator at lower temperature is lifted to a higher energy (Q_{con}) at the condenser. The use of a binary

mixture which needs energy to be supplied to the thermal exergy in order to separate the mixture is how the principle of a classical AHT works.

Up to date there are Fifteen (15) heat transformer operating in the Industrial plant worldwide (Ismal, 1989 and Jansen et al., 1987) of which the only mixture that was use commercially is the H_2O/ LiBr mixture. Although, water is an excellent refrigerant and lithium bromide (LiBr) is
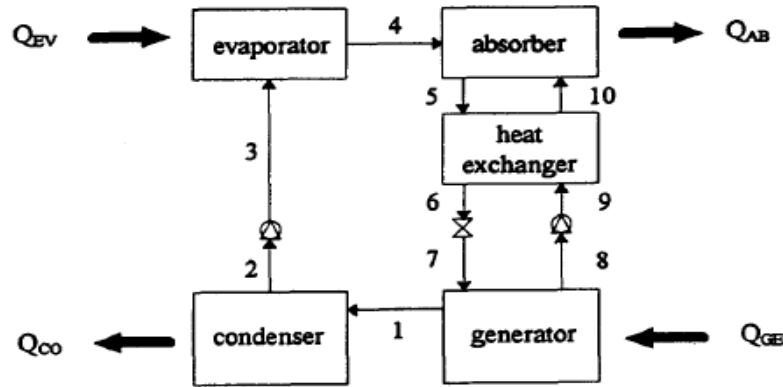
Rivera & Romero / Applied Thermal Engineering 1998)

Figure 3: Classical AHT

good absorbent and the mixture of the two gives higher affinity but however not, there are some major advantages of this working pair such as it has low working pressure and limited gross temperature lift (Sozen et al., 2006) and is limited by corrosion and crystallization in Industrial applications (Zhang and Hu, 2011). This led to more studies on the use of working pairs.

2.1.2   ADSORPTION DEMIXTION HEAT TRANSFORMER (ADHT)

Adsorption Demixtion Heat Pump was first proposed by Niang et al (1997) and set- up a laboratory scale pilot unit to observe the use of the combination of Water / furfural. Followed by Alonso et al (2002) who first use the absorption cycle by ADHT by using partially miscible mixture, n-heptane and N,N – dimethyl formamide (DMF) at low temperature to a new heat transformer by cooling down the mixture instead of the usual practice done in a separation step by a normal absorption heat transformer leading to low cost energy. He further developed and did simulation research on the use of Cyclohexane / Dimethyl Sulfate (DMSO) on 2002 & 2003. Another study was done by Noubli et al, 2011 which the study is about the simulation for the feasibility of study done by Alonso with working pair n – heptanes/ DMF and chosen to start to

validate the simulation code. The breakdowns of these studies are summarized in Table 1.Based on table 1 all of the results showed a significant improvement on the Coefficient of Performance (COP) of the working pairs.

ADHT has almost all the working components of a typical AHT: evaporator, absorber, generator, condenser, except that the distillation is replaced by a simple settler which make it less costly than the normal AHT. It works best on the partially miscible mixture by simply cooling down the mixture which it will then separates the mixtures into two (2) liquid phases without energy supply (Niang et al, 1997). This mixture exhibits two immiscible phases in thermodynamic equilibrium under low pressure. Comparison to the classical AHT which uses binary mixture of refrigerant and solvent (H_2O /LiBr) the way to separate the mixture is more energy costly as it uses distillation column to separate the mixture. The only energy consumption is the overall mechanical energy of the pump which is negligible.
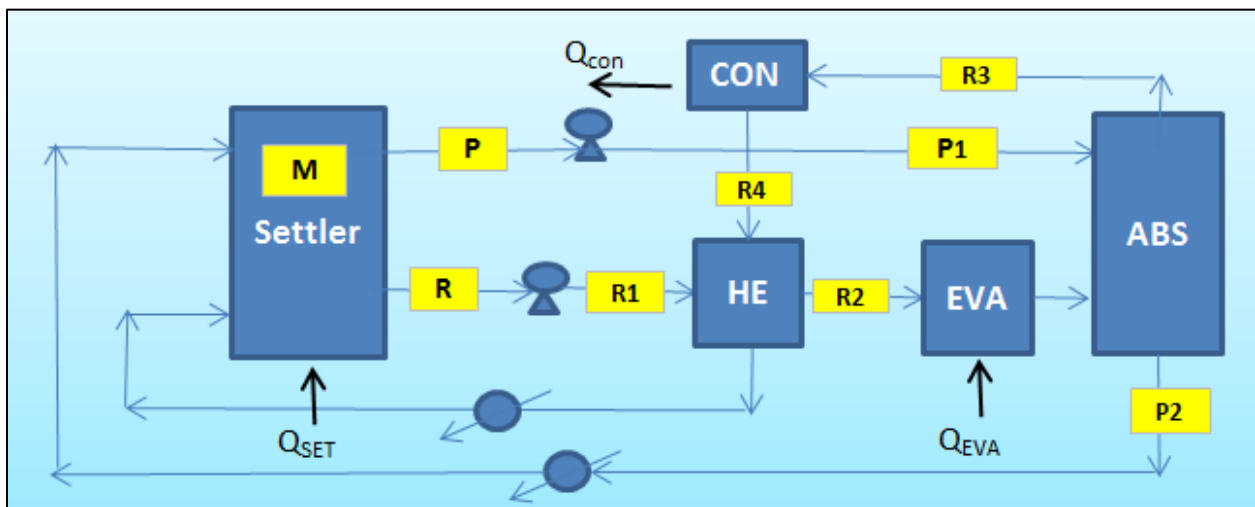
Figure 4: Schematic diagram of ADHT

2.1.2.1 BASIC CONCEPT

The use of a partially miscible mixture that exhibits a miscibility gap under the demixtion temperature is the driving force of ADHT. Based on Figure 4 the settler (M) where the cooling down of the mixture happens at a lower temperature heat sink is set to a temperature lower than the UCST of the mixture. The mixture will then splits into two separate liquid phases namely the Poor Phase (P) and the Rich Phase (R). Both P and R will be introduced to a pump (PU1 & PU2)

to a high pressure P1 and R1. The rich phase with the most volatile mixture will be introduce to the evaporator and will completely vaporized giving off R2 which is then introduce to the bottom of the absorber while, the poor phase is the raw material of the top of the column of the absorber. The classical absorber used in typical AHT is replaced by a reverse rectification column or a counter-current packed column as defined by Le Goff et al, 1998 to better achieve the mixing operation. The mixing of the mixtures once again takes place in the absorber. The leaner vapor R3 exits at the top of the column and enters the condenser and gives of the useful upgraded heat (Q_C) which determines the efficiency of ADHT. The enriched liquid R4 exiting at the bottom of the column and the saturated P2 are depressurized down to a pressure Ps and cooled down to Ts at the separator which will complete the cycle.

2.1.2.2 CRITERIA OF THE SUITABLE MIXTURE

The suitability of the working mixtures to be used in ADHT has to be taken into account. The choice of mixture should be as less toxic and less explosive as possible. The chosen mixtures are the three (3) pairs:

- Water / Furfural
- N- heptanes / DMF
- Cyclohexane / DMSO

These mixtures present a miscibility gap with their respective UCST (Figure 3). The mixture has relatively large difference of the boiling point of each pair (table 2). Moreover, these mixtures have different chemical functions and the Vapor-liquid equilibrium (VLE) and Liquid-liquid equilibrium should not intersect (Zemlyanskaya et al, 1977).

Table 2: Boiling point differences of the mixtures

Pair No	Chemicals	Boiling Point (^{O}C)	Boiling point difference
1	Furfural	161.7	61.72
	Water	99.98	
2	N-heptane	98.4	53.6
	DMF	152	
3	Cyclohexane	80.74	108.26
	DMSO	189	
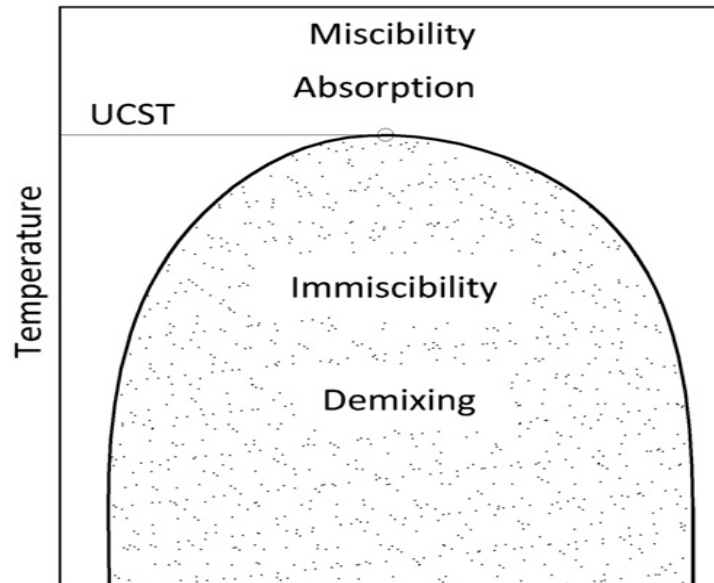
Figure 5: The phase curve of UCST

2.1.3   OPERATING PARAMETERS

2.1.3.1 INTERNAL TEMPERATURE LIFT (Δ T_i)

It is define as the qualitative measurement of the heat upgrading process and the sole difference between the condenser inlet and the evaporator outlet with the given formula:

$$\Delta T_i = T_{con} - T_{eva}$$

2.1.3.2 THERMAL EFFICIENCY (ηth)

It is define as the quantitative performance of the machine which is the ratio of the upgraded useful heat recovered from the condenser to the waste heat supplied to the evaporator.

$$\eta th = \frac{1-\frac{T_{DEC}}{T_{EVA}}}{1-\frac{T_{DEC}}{T_{CON}}}$$

Thermal efficiency is also known as the Coefficient of Performance (COP).

CHAPTER 3: RESEARCH METHODOLOGY

3.1.0   WORK PROCESS FLOW

```
┌─────────────────────────────────────┐
┆  Study related materials and identify the  ┆
┆                problem                ┆
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
┆ Estimate the project scope and identify project ┆
┆                objectives             ┆
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
┆          Collect Data Information      ┆
┆      e.g (Working pairs, Parameters)   ┆
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
┆            Design Planning             ┆
└─────────────────────────────────────┘
                    │
                    ▼
                  ╱Run╲
                 ╱ simulation ╲ ◄──────────────┐
                  ╲       ╱                     │
                    │                           │  NO
                    ▼                           │
┌─────────────────────────────────────┐         │
┆   Is the results enough for calculations?  ┆─────┘
└─────────────────────────────────────┘
                    │ YES
                    ▼
┌─────────────────────────────────────┐
┆           Matlab Calculations          ┆
└─────────────────────────────────────┘
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┆          Results and Conclusions       ┆
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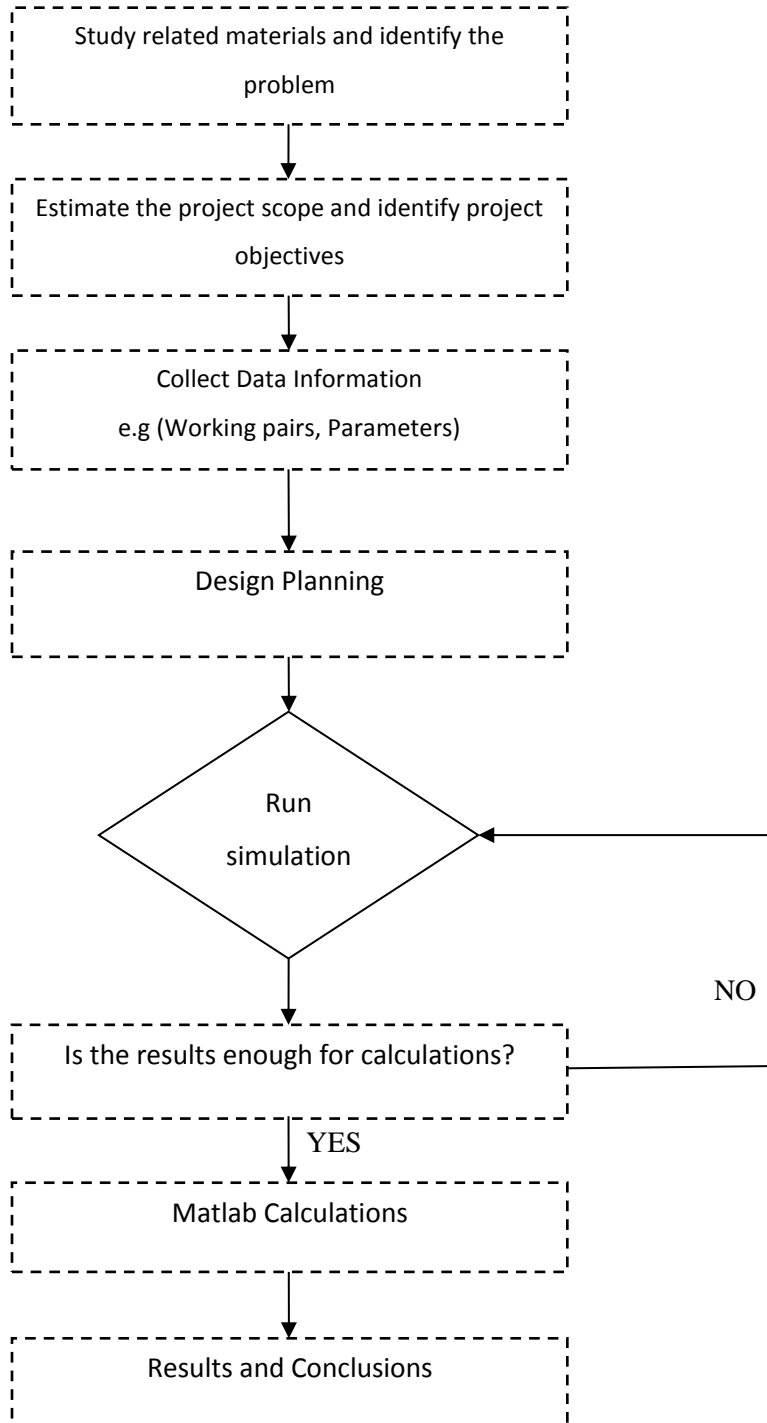
3.1.1 TOOLS

The aid of Hysys simulation and Matlab calculations are used in able to assist in the operating parameters for the Absorption Heat Transformer Demixing Heat Transformer.

GANTT CHART

Semester 2/ FYP 2	May			June					July					August				
	W1	W2	W3		W4	W5	W6		W7	W8	W9	W10	W11		W12	W13	W14	W15
	13-17	20-24	27-31	3-7	10-14	17-21	24-26	27-30	1-5	8-12	15-19	22-26	29-31	1-2	5-9	12-16	19-23	26-30
1. Experimental work	■	■	■	■				MID SEM BREAK									Study & Exam Week	
2. Submission of Progress Report							■											
3. Preparation for documentation					■	■	■		■	■	■	■						
4. Pre-Sedex										■								
5. Submission of Draft Report											■							
6. Submission of Dissertation (soft bound)												■						
7. Submission of Technical Paper												■						
8. Oral Presentation													■	■				
9. Submission of Dissertation (hard bound)																■		

3.1.2 PROJECT ACTIVITIES

3.1.2.1 DATA INTERPRETATION

Thermodynamic calculations are determined by the use of vapor-liquid equilibrium (VLE) Raoult's and Henry's Law. Input values of the mixtures are based on the experimental values obtained from various studies (Alonso et al, 2002, 2003, Niang et al, 1997, Noubli et al, 2010) and by the help of Aspen HYSYS (using UNIQUAC Model) the mass fractions, enthalpies and other parameters were determined for each pair of chemicals which are breakdown on Table 3 and Table 4.

Table 3: The Demixtion temperature and the working pressure of the mixtures

No	Chemicals	Working Pressure (bar)	Demixtion Temp (^{O}C)	Reference
1	Furfural	0.073		Niang et al, 1997
	Water		40.2	
2	N-heptane	1.01325	73.8	Quitzch et al, 1969
	DMF		53	Noubli et al, 2010
3	Cyclohexane	3.1	20±	Alonso et al, 2002
	DMSO			

Table 4: Operating conditions of the mixtures at the Settler

Chemicals	Settler			Mass Enthalpy (H) kJ/kg	Heat Capacity (kJ/kgmole.C)	Heat of Vaporization (kJ/kg.mole)
	Pressure (bar)	Temperature (T)				
		K	C			
Cyclohexane/ DMSO	3.1	293.15	20	-2238	146.9	4.53E+04
N-heptane/ DMF	1.01325	293.15	20	-2757	179.8	3.96E+04
Water/Furfural	0.073	313.35	40.2	-7693	53.63	4.55E+04

Based from Niang et al, 1997 with the following steps and formula the calculation theory will be solve. In the settler, the mixture M is separated by simple cooling down splitting into two liquid phases which are the poor and the rich phase. Point M can be determined through:

1.

$$M = R + P \tag{1}$$

$$M * X_M = R * X_R + P * X_P \tag{2}$$

$$M * h_m = R * h_R + P * h_P \tag{3}$$

Where h_m, h_R, h_P are the enthalpies of M, R and P respectively.

2. R and P are introduced to pump to a high pressure P_m and will give of:

$$R_1 = R \ \ and \ P_1 = P \qquad\qquad (4)$$

$$W_P = P \left[\frac{P_m}{\rho_{m(xR)}} - \frac{P_S}{\rho_{m(xR)}} \right] \qquad\qquad (5)$$

$$W_R = R \left[\frac{P_M}{\rho_{m(xR)}} - \frac{P_S}{\rho_{S(xR)}} \right] \qquad\qquad (6)$$

Where $\rho_{m(xR)}$, $\rho_{S(xR)}$ are respectively the densities of the rich phase at P_m and P_s in $\frac{kg}{m^3}$.

3. The evaporator feed is the phase R_1 and when completey vaporized will then be the feed to the bottom of the absorber.

$$R_1 = R \qquad\qquad , \qquad\qquad (7)$$

$$y_1 = x_{R1} \qquad\qquad (8)$$

$$Q_e = R * (H_R - h_{R1}) \qquad\qquad (9)$$

Where H_R and h_{R1} are the respectively, the enthalpies of vapor R and the liquid R_1.

4. In the absorber, the mixing of the vapor R_1 with P_1 in a counter current is happening to give the vapor phase P_2 at the top of the column to be condensed in the condenser and the liquid phase R_3 leaving at the bottom of the column to be recycled back to the settler.

$$M = P_1 + R \qquad\qquad (10)$$

$$x_m = \frac{P_1*X_{P1}+R_1 *x_{R1}}{P_1+ R_1} \qquad\qquad (11)$$

$$h_m = \frac{P_1 hp1+R_1 xR1}{P_1+R_1} \qquad\qquad (12)$$

The absorber will give off the following sets of equations :

$$R_3 + P_2 = M \qquad\qquad (13)$$

$$R_3 * x_{R3} + P_2 * y_{P2} = M * x_m \qquad\qquad (14)$$

$$R_3 * h_{R3} + P_2 * Hs_{,P2} = M * h_m \qquad\qquad (15)$$

Where P_2 is at the boiling conditions: $Hs_{,P2}$ is the enthalpy of the vapor at y_{P2}.

5. On the top of the absorber the leaving vapor P_2 will enter to the condenser to give of Q_{CON}, the useful upgraded heat.

$$P_3 = P_2 \tag{16}$$

$$x_{P3} = y_{P2} \tag{17}$$

$$Q_{CON} = P_2 * Hs_{,P2} - P_3 * hs_{,P3} \tag{18}$$

Where P_3 is at bubble conditions and the enthalpy $hs_{,P3}$ of the saturated liquid at $x_{P3} = y_{P2}$.

6. To close the loop the recycle of P_3 and R_4 are depressurized and set to the demixtion temperature of the settler and one again the cycle will begin.

$$P_3 = P_4 \tag{19}$$

$$x_{P3} = x_{P4} \tag{20}$$

$$Q_{P3} = P_3 * hs_{,P3} - P_4 * hs_{,p4} \tag{21}$$

$$R_3 = R_4 \tag{22}$$

$$x_{R3} = x_{R4} \tag{23}$$

$$Q_{R3} = R_3 * h_{R3} - R_4 * h_{R4} \tag{24}$$

$$R_4 + P_4 = M_1 \tag{25}$$

$$R_4 * h_{R4} + P_4 * h_{P4} = M_1 * x_{M1} \tag{26}$$

$$x_{M1} = x_M \tag{27}$$

Where Q_{P3} and Q_{R3} are the heat amounts at the exchanger.

CHAPTER 4: RESULTS AND DISCUSSION

4.1.0   THERMODYNAMIC DATA

4.1.1   VAPOR LIQUID EQUILIBRIUM (VLE) AND LIQUID-LIQUID EQUILIBRIA (LLE)

The VLE and LLE data are taken from the properties given by Hysys. UNIQUAC model has been chosen and parameter of each pairs of mixtures has been clearly given by the simulation. Other thermodynamic properties such as enthalpies, molar flow, feed flow, molar fractions are all taken from the Aspen Hysys. Experimental data from literatures are taken into account and altered to be able to fully study the behaviors of the mixtures. The UNIQUAC is used in order to describe the phase behavior of the multicomponent mixtures, the entropic contribution and the intermolecular forces that are responsible for enthalpy of mixing.

4.1.3   EVALUATION OF THE PERFORMANCE

4.1.3.1 THERMAL YIELD VERSUS TEMPERATURE LIFT

Thermal Yield or knows as the Coefficient of Performance (COP) has been observed as the quantitative performance of an ADHT. It can be calculated by the ratio of the upgraded useful heat from the inlet of the condenser over the waste heat supplied at the outlet of the evaporator with respect to the temperature of the decanter. Figure 6 shows the results for water-furfural mixture. Reflected results from table 5 which shows the highest lift of 8.4 and with the highest thermal yield of 0.998. An increase of the temperature lift gives decreasing values for thermal yield. For the case of N-heptane and DMF the highest temperature lift is about 5.7 ^{O}C with the highest thermal yield of 0.3 (table 6). Whilst, for cyclohexane and DMSO the highest temperatures lift (Figure 8) is 36 ^{O} C. There is a good temperature lift between temperatures of the evaporator outlet of 210 and 208 ^{O}C with respect to the temperature inlet of condenser of 240 and 240 ^{O} C shown in table 7.

Table 5: Water-furfural temperature lift and thermal yield results

T_{eva} (outlet)	T_{con} (inlet)	$\Delta T = T_{con} - T_{EVA}$	$\eta th = (1 - (T_{DEC}/T_{EVA})) / (1 - (T_{DEC}/T_{CON}))$
100	100.2	0.2	0.995
100	100.1	0.1	0.998
99	102.2	3.2	0.975
99.8	108.2	8.4	0.977
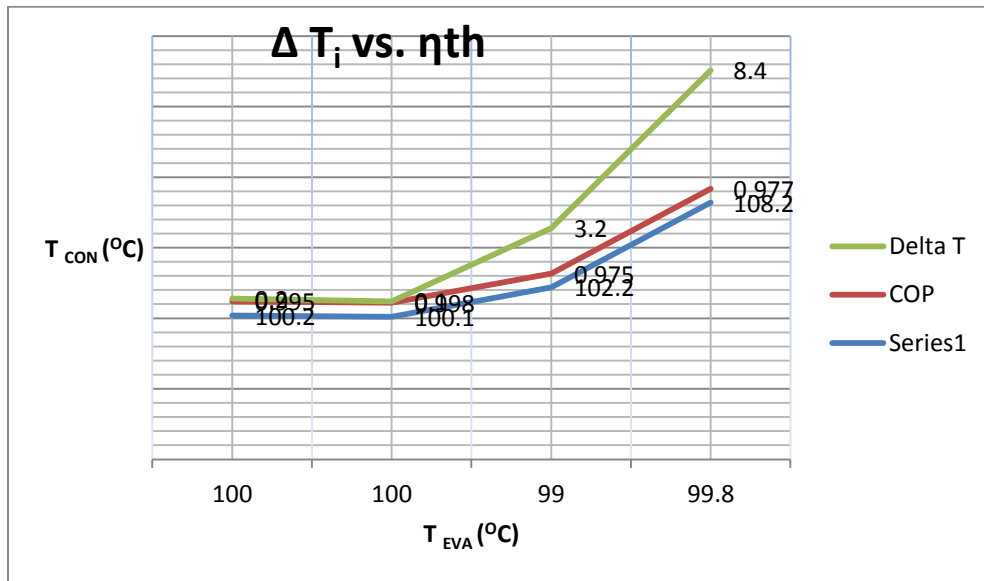
Figure 6: Thermal yield versus temperature lift for water –furfural
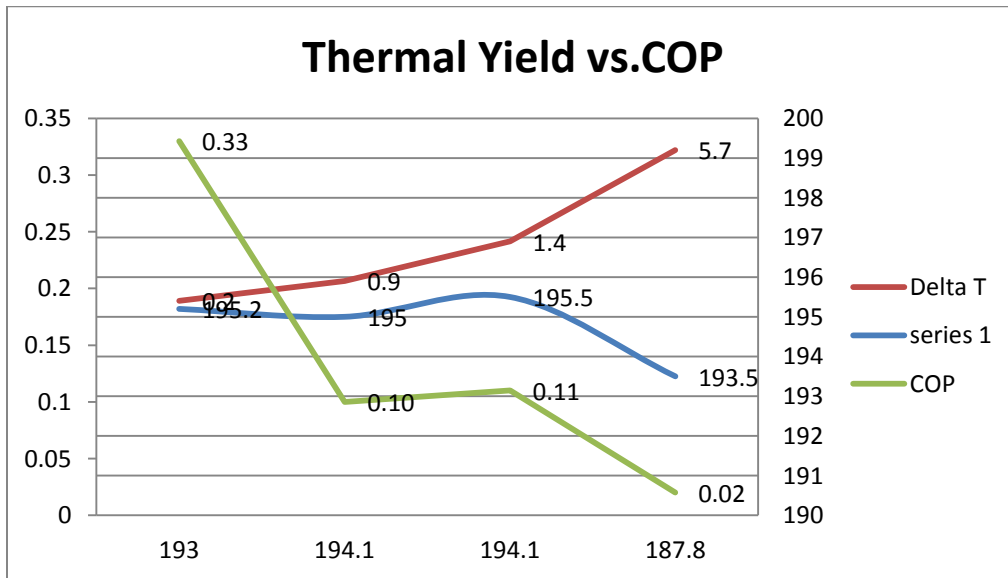
Figure 7: Thermal yield with respects to temperature of the evaporator and condenser

Table 6: N-heptane –DMF thermal yield and temperature lift results

T $_{eva}$ (outlet)	T$_{con}$ (inlet)	$\Delta T = T_{con} - T_{EVA}$	$\eta th = \ (1-\ (T_{DEC}/\ T_{EVA})\ )/ \qquad (1-(T_{DEC}/T_{CON}))$
193	195.2	0.2	0.33
194.1	195	0.9	0.10
194.1	195.5	1.4	0.11
187.8	193.5	5.7	0.02

Table 7: Cyclohexane –DMSO thermal yield and temperature lift results

T $_{eva}$ (outlet)	T$_{con}$ (inlet)	$\Delta T = T_{con} - T_{EVA}$	$\eta th = \ (1-\ (T_{DEC}/\ T_{EVA})\ )/ \qquad (1-(T_{DEC}/T_{CON}))$
210	246	36.0	0.792
208	240	32.0	0.806
200	215	15.0	0.850
180	185.7	5.7	0.905
179	180	1.0	0.998
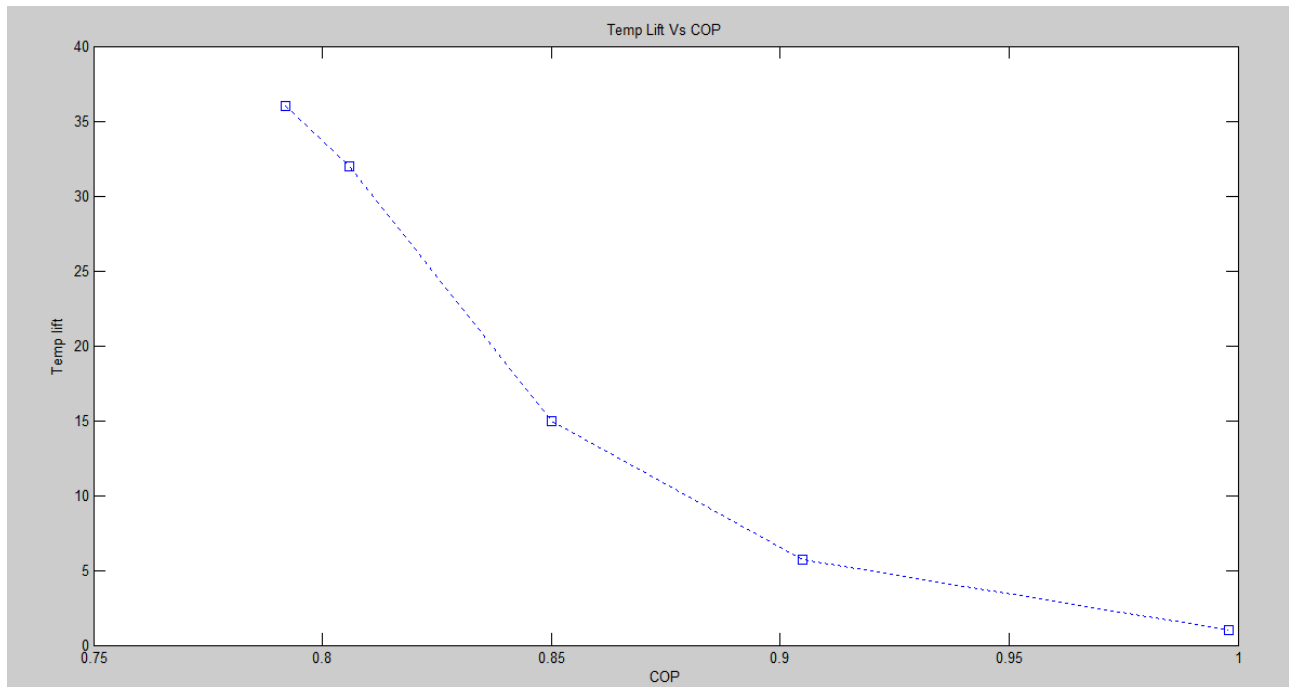
Figure 8: Thermal lift and thermal yield of cyclohexane and DMSO

The demixing temperatures are also the temperatures for the decanter and the outlets of the rich and the poor phase. Figure 9 is the result for the mixture water-furfural. The temperature lift gradually increases when the demixing temperature increases. It is important to understand the demixing temperature as this is the feed and main thing that causes the separation of the two pairs of mixtures. The outlet R and P has the same temperature with the demixing (T_P and T_R = T_{demix}). The working mixtures water/furfural, n-heptane/DMF and cyclohexane/DMSO are found to be an azeotrope mixture that behaves according to a certain temperature at a certain composition hence the behavior of an azeotrope is greatly hard to separate. The concentrations of the absorbent and refrigerant behaves differently and it has been observed that when demixing temperature increases the absorbent increases gradually while refrigerant decreases slowly or remain the same on some points. When the composition of the refrigerant increases the temperature of T_{R1} (figure 4) will increases first until it reaches its maximum azeotropic composition. When T_{demix} increases the absorbent will have a steeper curve of the dew point and which will give rise to the enthalpy and temperature lift. R_3 coming out from the top of the absorber (figure 4) will move in lower fractions which will lead to a small increase of T_{R3}. The small increase of T_{R3} while T_{R2} is decreasing coming from the outlet of the evaporator will give rise to an increase of the T_{demix}. If T_{R2} is increasing it cannot combat with the slow increase of T_{R3} thus lead to a small internal temperature lift. Consequently, T_{P1} which is the feed to the top of the absorber will also affect the temperature lift. If T_{P1} is high there will be more vapor which is dedicated for absorption in the absorber which is then used to heat the liquid up to its boiling temperature in the absorber hence will give rise to richer vapor for the absorbent coming out at the top of the absorber (T_{R3}) and thus will lead to higher temperature lift.

For water-furfural at the point of 100 ^{O}C the compositions of the absorbent started to fall and the rich phase starts to rise sharply. This is where the limitations of the temperature of mixing. Figure 10 shows for cyclohexane and DMSO which at temperature beyond $T_{demix} > 210$ ^{O}C the compositions started to reach zero. For n-heptane –DMF in figure 11 shows that beyond Temperature 190 ^{O}C the temperature lift will gradually dispersed and decreases to negative values or zero.
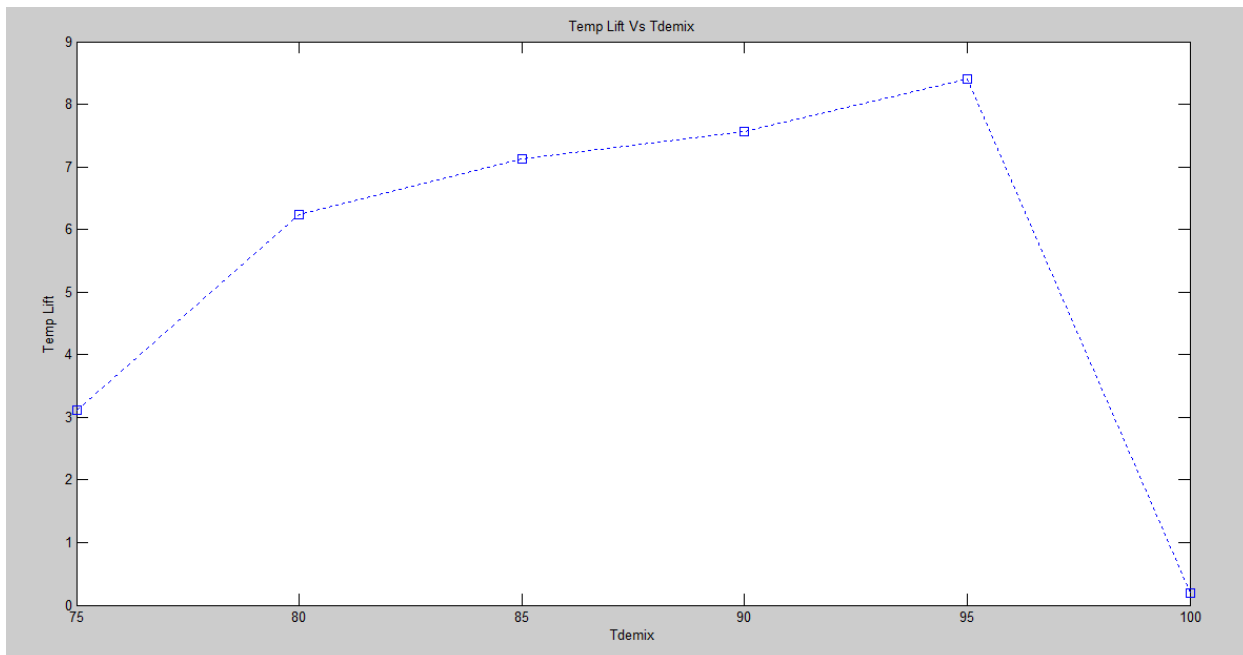
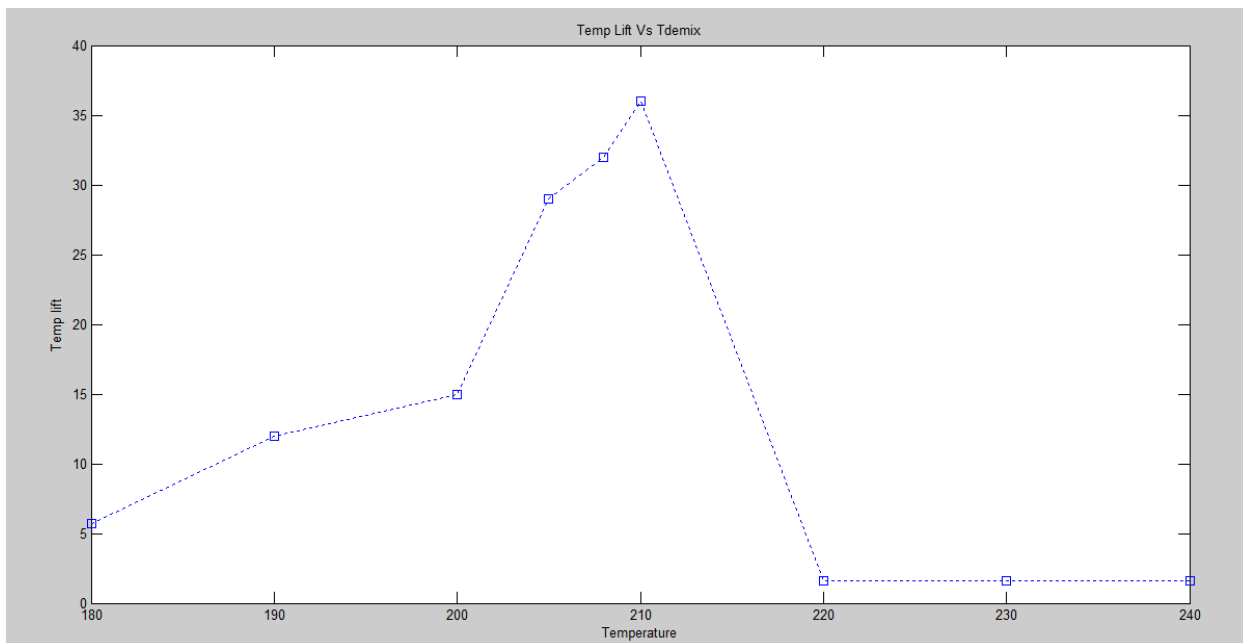**Figure 9: Water-furfural demixing temperature and temperature lift**

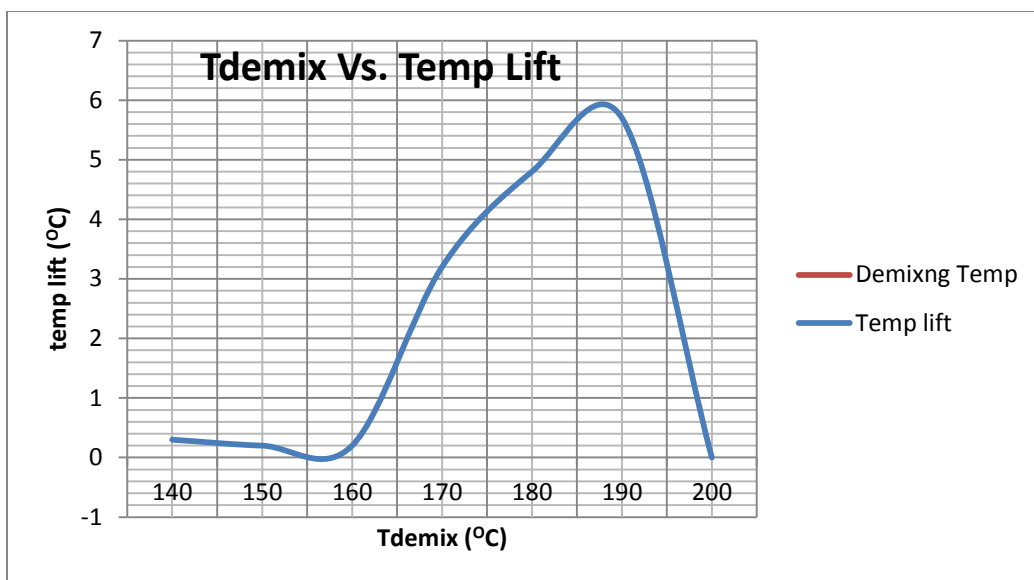**Figure 10: Cyclohexane and DMSO demonstration of demixing temperature**

Figure 11: N-heptane and DMF demixing temperature and temperature lift

4.1.4 INFLUENCE OF OPERATING PARAMETERS TO TEMPERATURE LIFT

4.1.4.1 INFLUENCE OF MOLAR ENTHALPY

There is an interesting significant effect of molar enthalpy of the refrigerant and absorbent to the demixing temperature. Figure 12 shows the results obtained for the mixture of water –furfural as the effect of enthalpy to demixing temperature. It is noticeable that when a higher demixing temperature occurs there is an increase of the absorbent's molar enthalpy (furfural) and a decrease of the refrigerant (water) which greatly affects the temperature lift. The contribution of the enthalpy shows the shape of the dew curve of the mixture (Figure 13). The substance with the higher boiling temperature (absorbent) will have less vapor concentration compared to the lesser boiling temperature (refrigerant). The absorbent with its least vapor concentration will give off a steeper dew point curve. The dew point of a vapor is where the first liquid drop is formed. It would give rise to the maximum demixing temperature and hence increase temperature lift. Figure 14 shows the results for N-heptane and DMF. The behavior of its absorbent (DMF) and refrigerant (N-heptane) shows a little bit similar values this is because of the azeotrope behavior during mixing. It is still obvious to observe that there is a better increase of enthalpy of the DMF. Furthermore, for cyclohexane and DMSO pair the absorbent which is DMSO shows an increase of enthalpy with the demixing temperature (Figure 15).
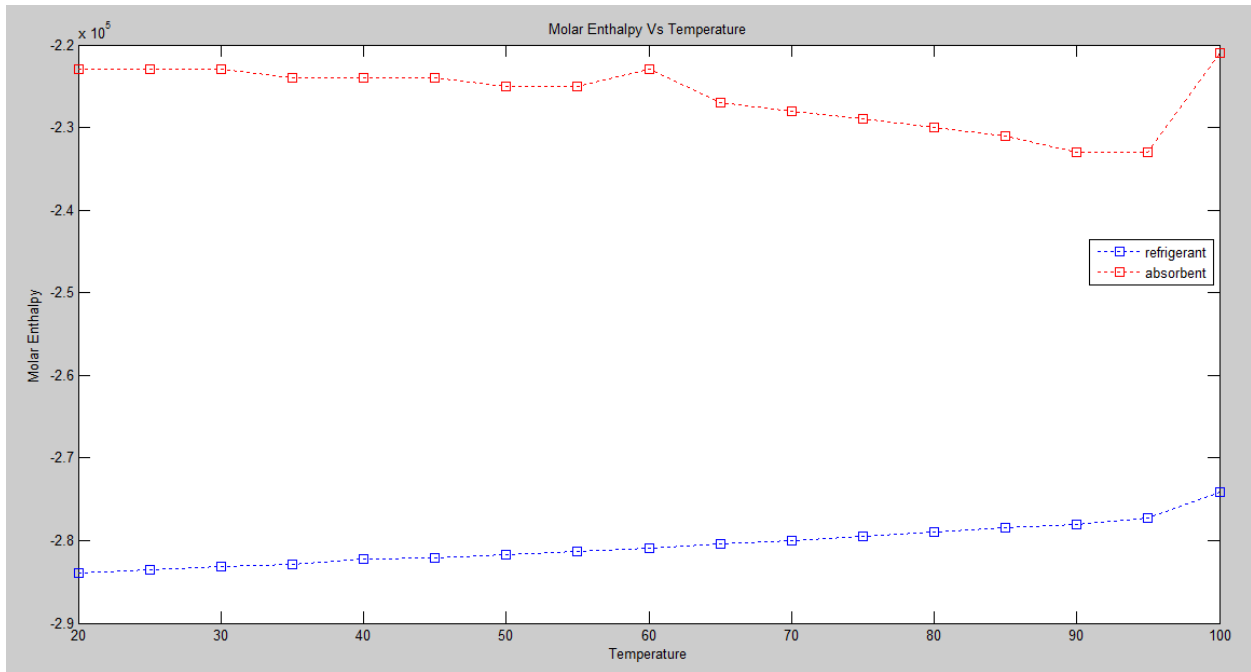
Figure 12: Molar enthalpy effect on demixing temperature for water –furfural
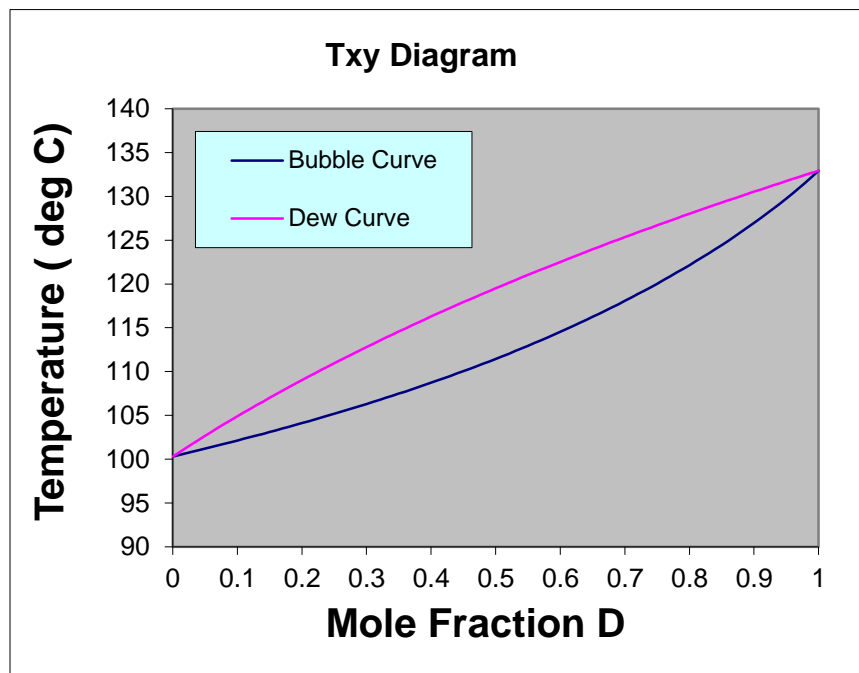
Figure 13: The dew point –bubble point curves of water-furfural
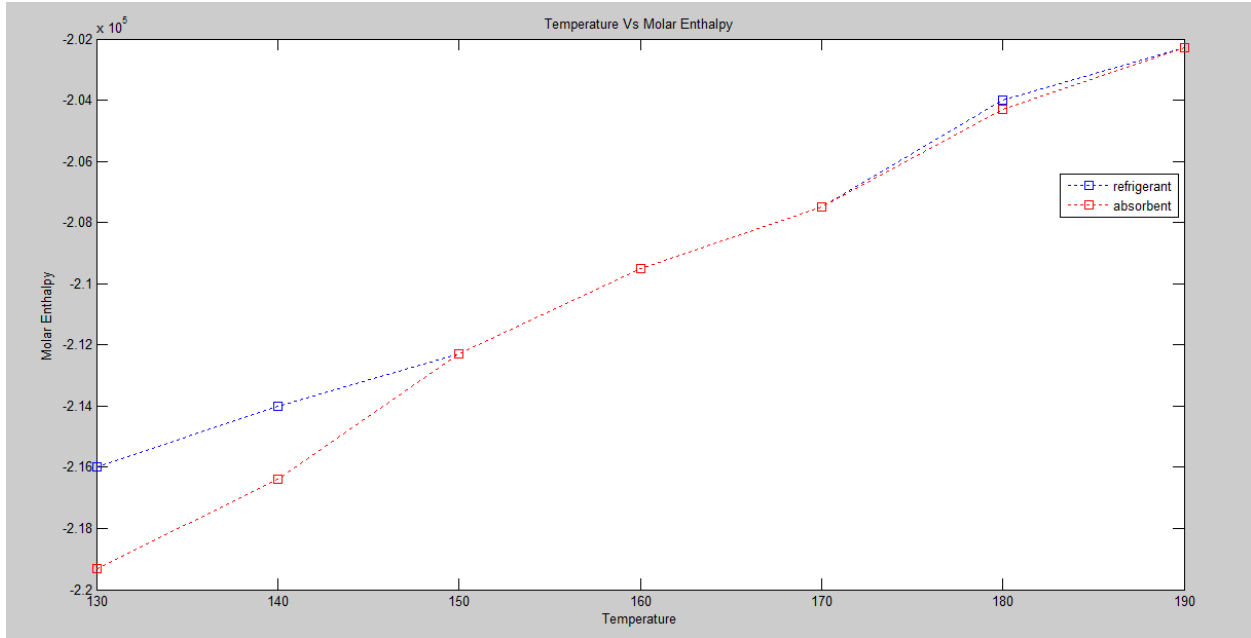
Figure 14: Molar enthalpy and demixing temperature of N-heptane-DMF
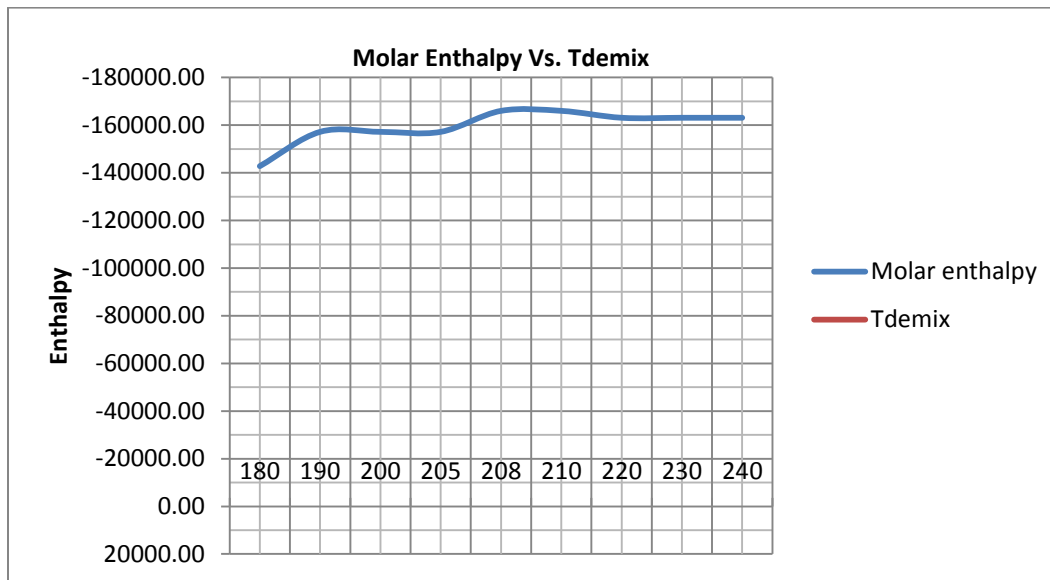
Figure 15: Molar enthalpy of the absorbent of cyclohexane-DMSO

4.1.4.2 INFLUENCE OF MOLE FRACTIONS

The enthalpy of the absorbent strongly affects the temperature lift and seemingly mole fractions will also contribute to higher dew curve and an increase of enthalpy will give rise to higher dew point for lower molar fractions. The increase of refrigerant's mole fraction will still give rise to demixing temperature but not as much as the absorbent's increase mole fractions since refrigerant helps to increase dew enthalpy for higher mole fractions which makes the dew curve less steeper. Figure 16, 17 and 18 shows the graph for

water-furfural, n-heptane –DMF and cyclohexane-DMSO respectively. It shows that at 99 ^{O}C the highest molar fraction is 0.469 for water. At temperature 190 ^{o}C for DMF the highest mole fraction given is 0.9125 and for DMSO is at 240 ^{O}C for 0.9026.
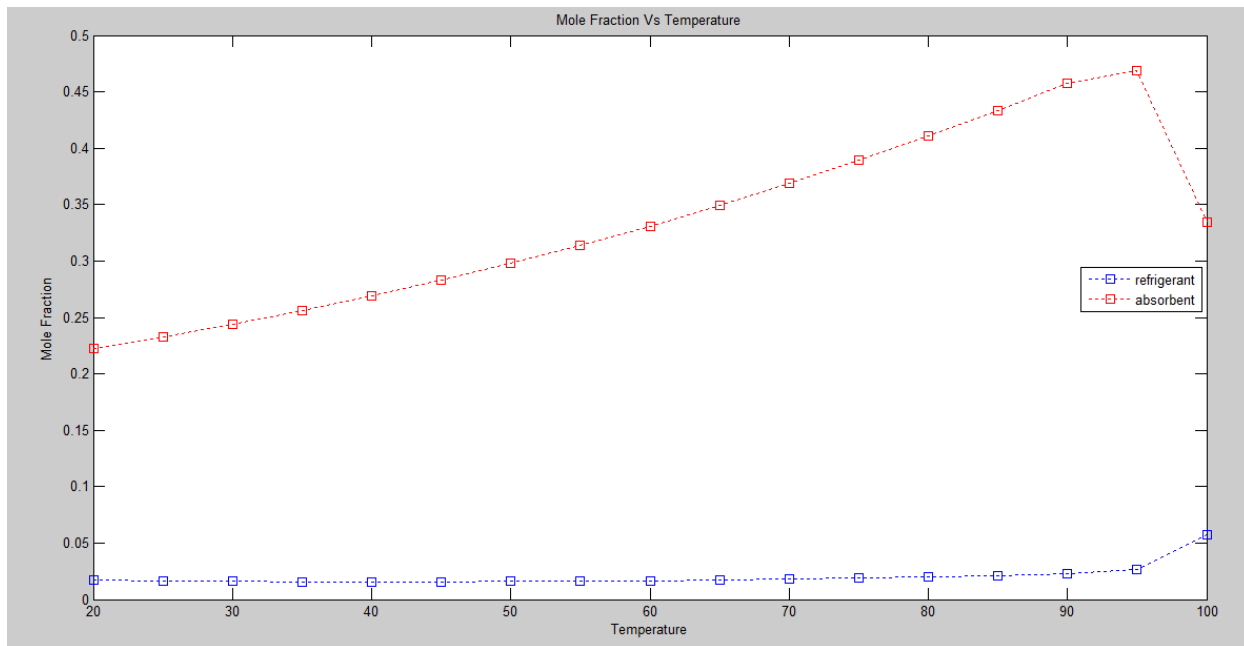
Figure 16: Mole fractions and demixig temperature of water -furfural
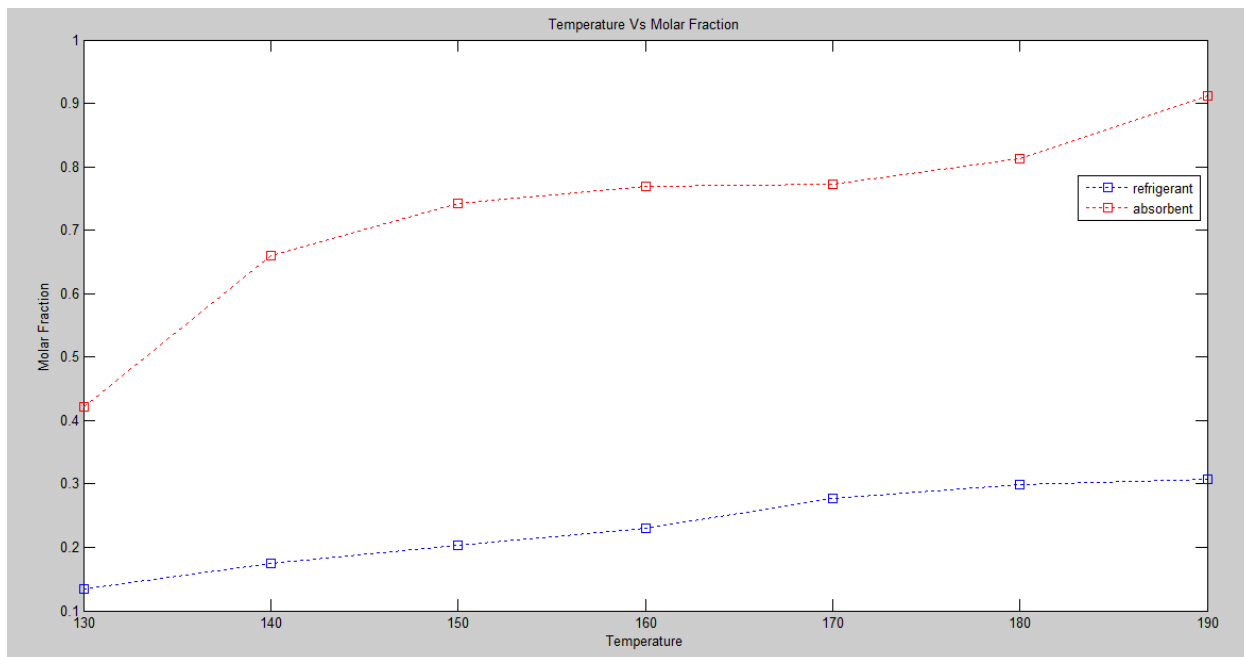
Figure 17: N-heptane –DMF mole fractions and demixing temperature
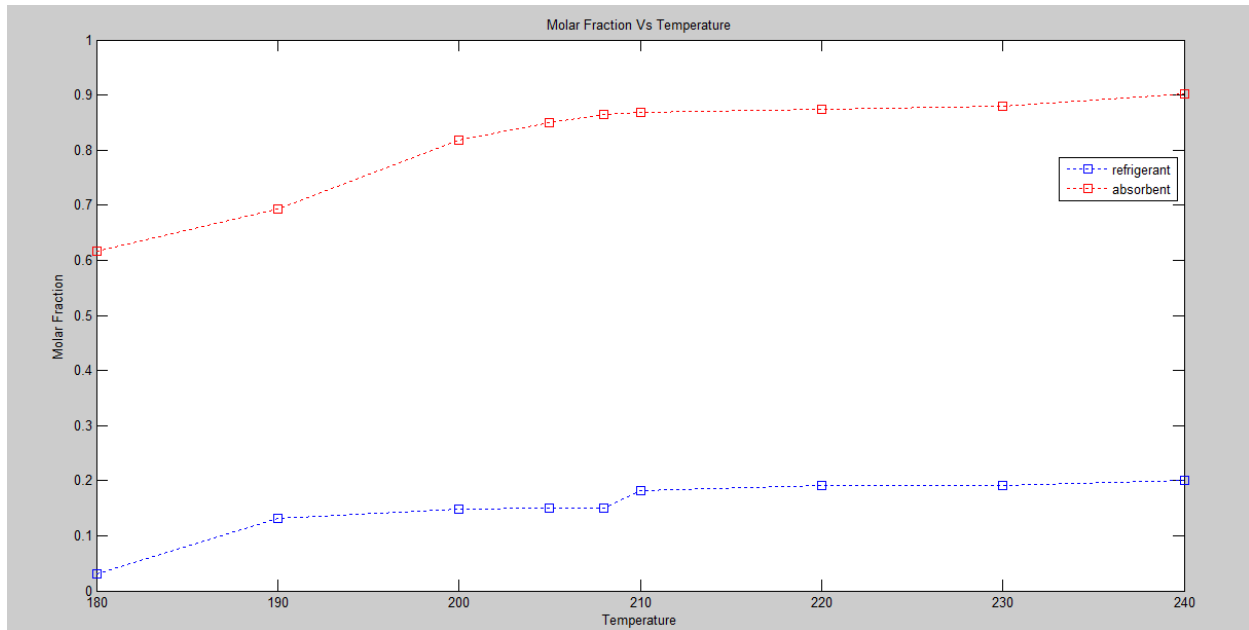
Figure 18: Cyclohexane –DMSO mole fractions and demixing temperature

4.1.4.3 INFLUENCE OF MOLAR FLOW

The molar flow also takes part in the influence of the temperature mixing. The absorbent gradually increases at certain temperature until it reaches the limitations of its mixing for the case of water at 100 ^{O}C the molar reaches zero. The refrigerant however demonstrated a decrease value while the temperature of the decanter is increasing. The increase of the absorbent's molar flow greatly affects the temperature mixing of the mixtures inside decanter. The higher the temperature in the decanter the higher is its temperature lift. Figure 19 shows the molar flow differences of furfural at different temperature level at the decanter. Above temperature of 190 ^{O} C there is zero flow inside decanter and would be hard to separate.
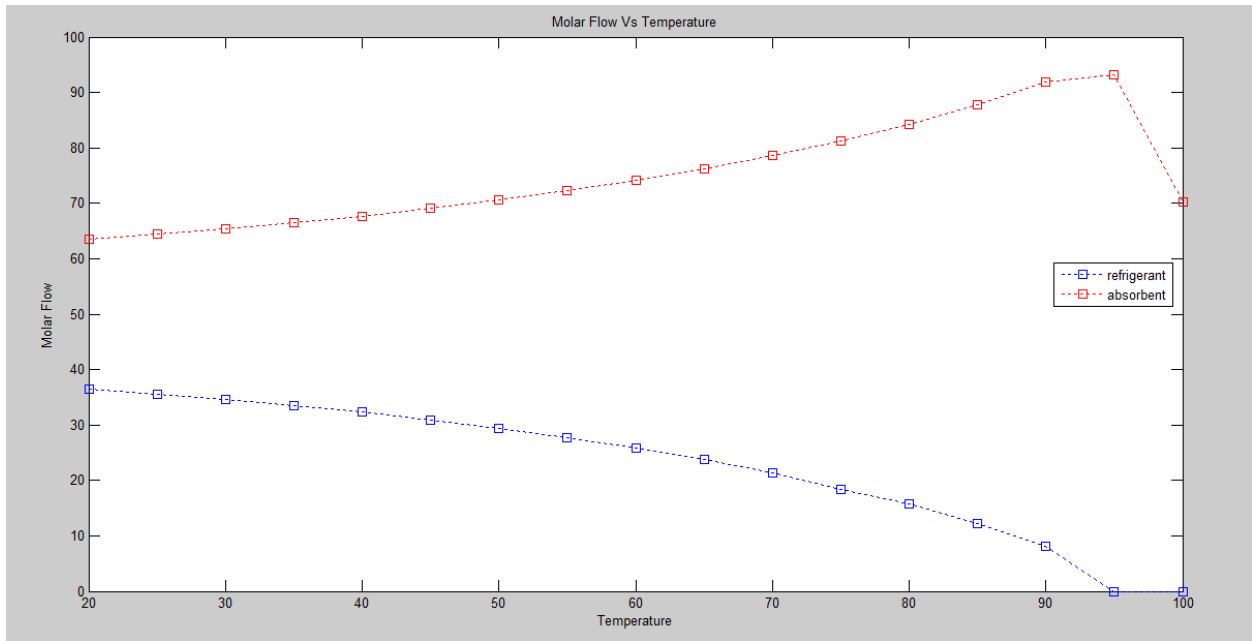
Figure 19: Molar flow of the rich and poor phase of water and furfural
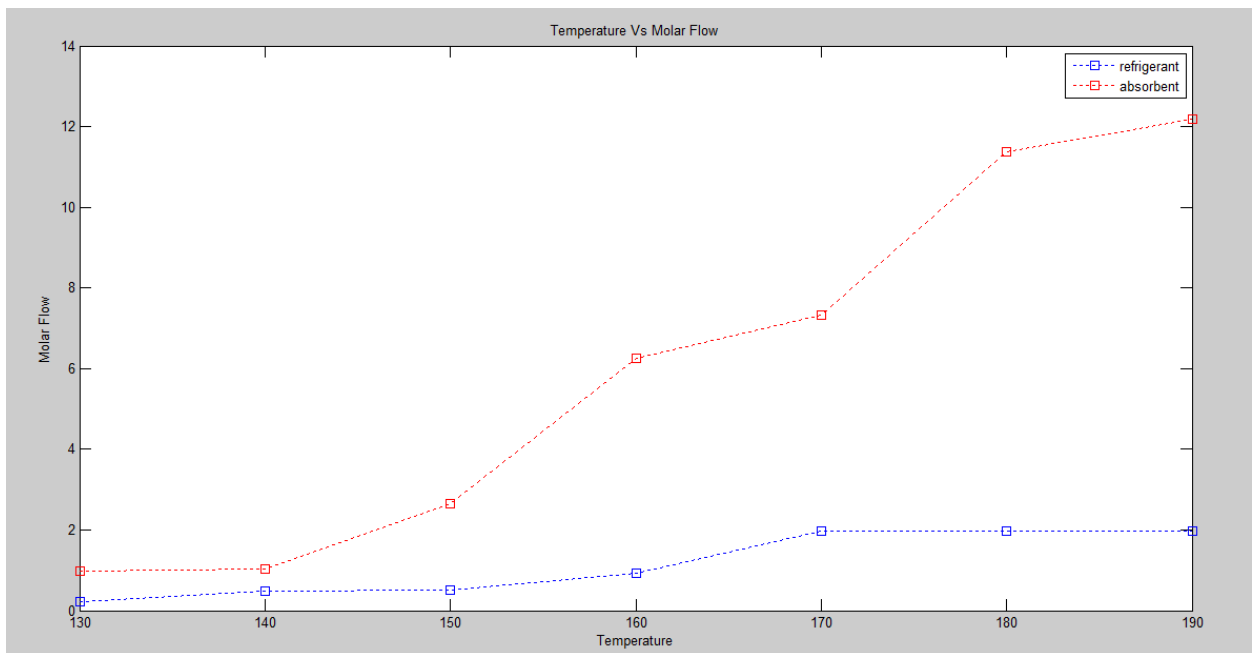
Figure 20: Molar flow of the rich and poor phase of N-heptane and DMF
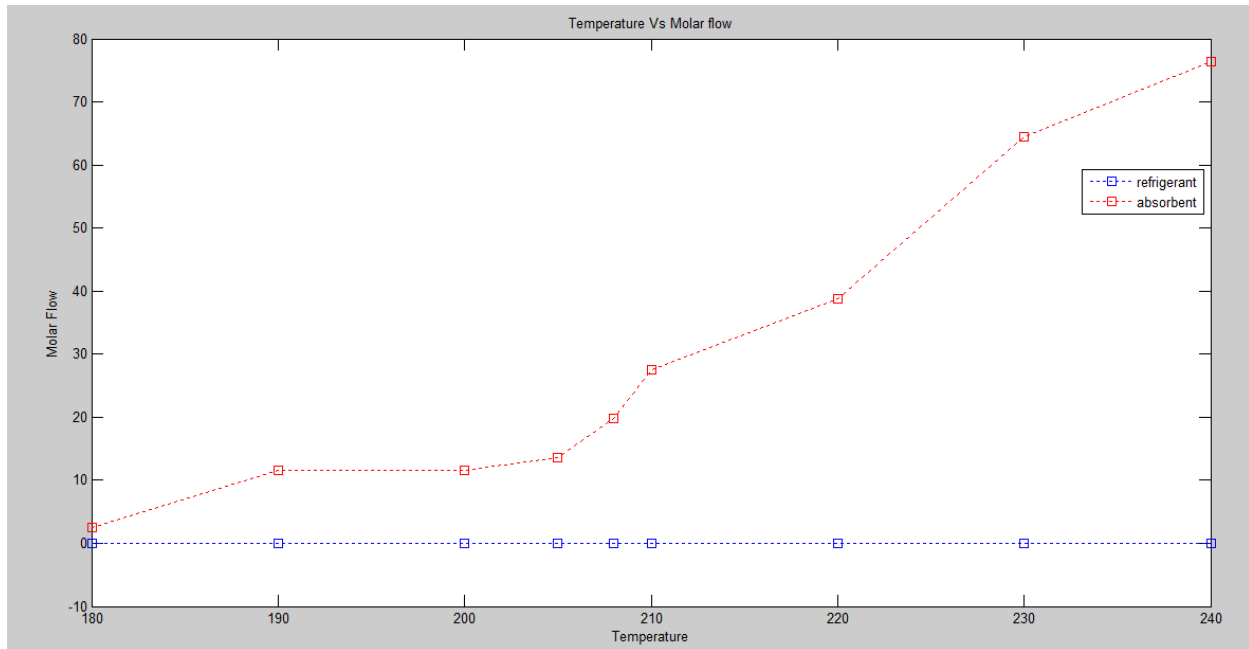
Figure 21: Molar flow in the decanter for cyclohexane and DMSO

The temperature of the T_{R1} is fixed and greatly dependent on the molar flow of the R in the decanter which affects the temperature lift. The minimum refrigerant fractions will obtain the highest temperature lift.
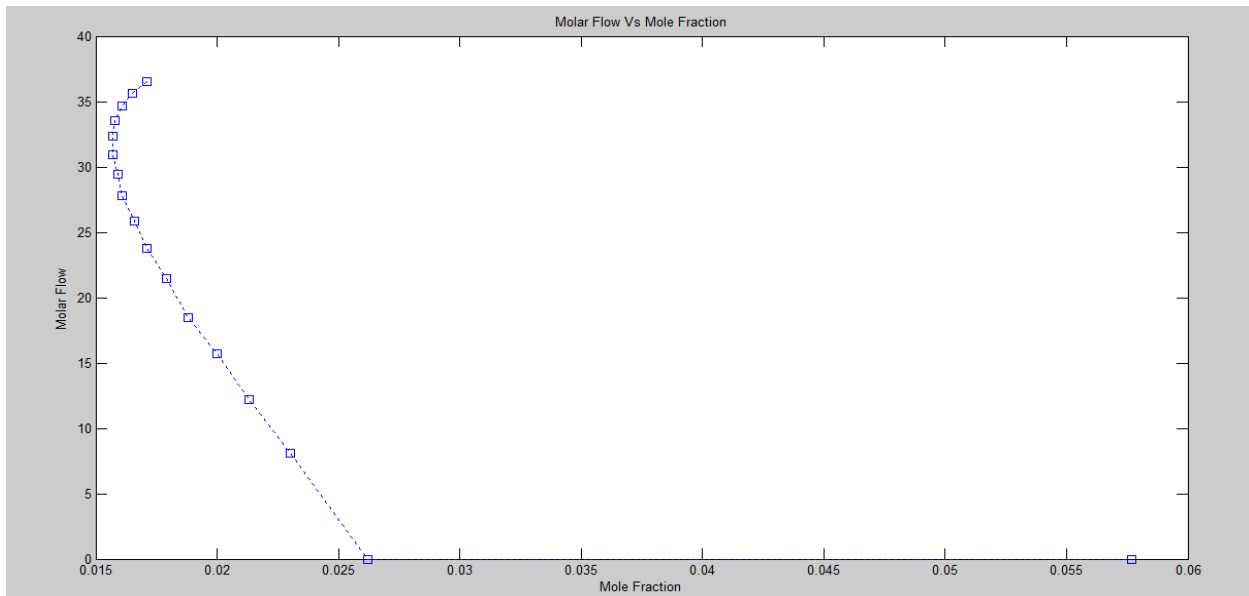

Figure 22: Molar flow and mole fractions of the rich phase furfural inside decanter
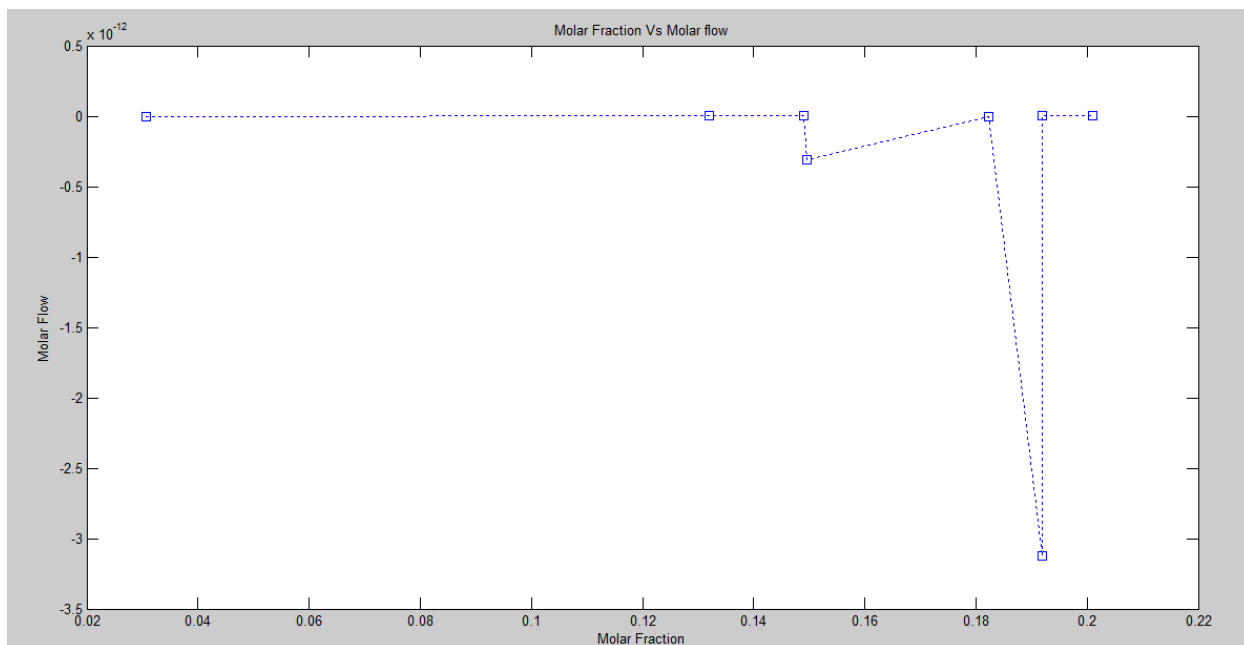
Figure 23: Molar flow of refrigerant cyclohexane inside decanter

Furthermore, the increase of the molar flow of the absorbent in the mixture will hardly separate for the refrigerant since it will enable to transfer more rich phase from the absorbent to the leaner vapor (rich phase) hence absorbent will increase while refrigerant decreases and so thus a higher temperature lift. For the case of DMF absorbent (figure 20) there exist a minimum values of refrigerant that will be constant for DMF. The same goes with DMSO (figure 21) respectively. For DMF it becomes constant between temperatures (170-190 ^{O}C) while for DMSO between (220-240 ^{O}C). Above these temperature with respect to its pressure values the molar flow of DMF and DMSO will become equilibrium with the absorbent. On the other hand, an increase of refrigerant will give decreasing values for molar flow which hinders the temperature lift shown on Figure 22 and 23 for furfural and cyclohexane respectively. Molar flow increases with increasing molar fractions in the absorbent (Figure 24) thus higher temperature lift.
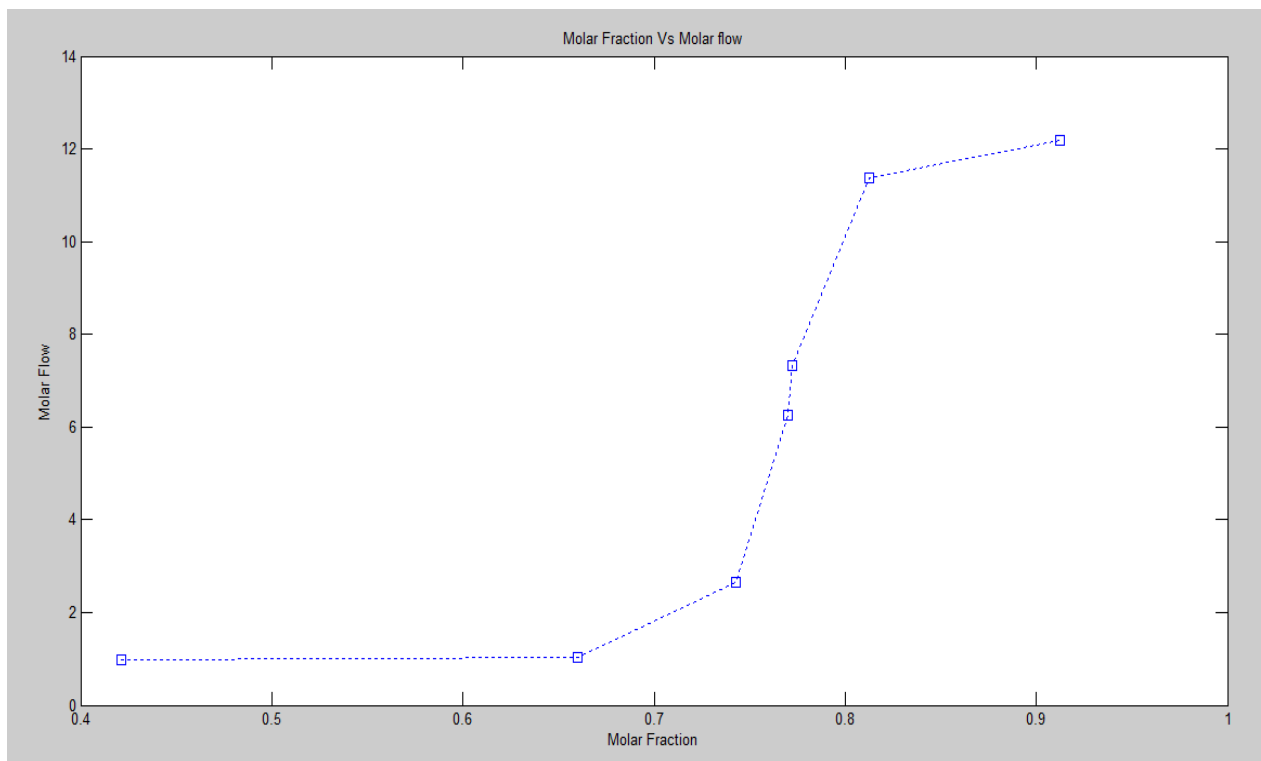
Figure 24: Molar flow of the absorbent DMF inside decanter

4.1.4.4 COMPARISON OF STUDIES

There have been studies done before for some authors working on different pairs of mixture and different fluid package. Table 8 shows different values of results such as for Niang et al and colleagues had started off for experimental studies of water and furfural using the DECHEMA experimental tables and have shown a thermal yield of 0.86 and a temperature lift of 25 K.

Table 8: Results of research studies

Author/Year	Pair of Chemicals	Fluid Package	Undertaken Research	Results		Simulation Results		
				Thermal Yield	Temp lift (K)	Thermal Yield	Temperature Lift (K)	Fluid Package
Niang et al,1997	Water-furfural	DECHEMA	Experimental	0.86	25	0.998	8.4	UNIQUAC
Alonso et al, 2002	N-heptane - DMF	NRTL	Experimental	0.93	8	0.333	5.7	UNIQUAC
Noubli et al, 2011	N-heptane-DMF	NRTL, FORTRAN 95	Simulation	0.4	12.4			

Privat et al,2013	N-heptane - DMF	NRTL	Simulation	-	1.18			
Privat et al,2013	Cyclohexane-DMSO	NRTL	Simulation	-	2.59	0.998	36	UNIQUAC
Alonso et al, 2003	Cyclohexane-DMSO	NRTL	Simulation	0.96	50			

Compared to the simulation results the experimental studies of Niang et al had shown a better lift because of the use of 2 or more heat exchangers in order to improve the performance by preheating the inlet of the absorber from the outlet. It is the same that goes to the studies done by Alonso et al, 2002 and 2003 by using two heat exchangers after the outlets of the decanter. The simulation results from UNIQUAC shows for N-heptane and DMF shows 5.7 lift while for Alonso et al was 8 K which is not so far. The simulation studies followed by Noubli et al, 2011 using the experimental data from Alonso shows an increase of 12.4 K for N-heptane and DMF while the simulation using flash drum instead of absorber by Privat et al,2013 shows the least results for thermal yield and temperature lift.

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS

4.1.1 CONCLUSION

Adsorption Demixtion Heat Transformer is an equipment that can upgrade low heat to high heat and is very helpful on solving the bottlenecks of energy depletion and as well as the great concerns of CO_2 emission. In comparison with the classical AHT which is commercially use in the industries, ADHT offers a more astonishing benefits such as it was found out to be simpler in design and less expensive. The possibility of changing distillation column of the classical AHT has been demonstrated.

The mixtures of water/furfural, n-heptane/DMF and cyclohexane/DMSO are suitable to be used in an ADHT. The pair of mixture of cyclohexane and DMSO demonstrated the highest temperature lift of 36 K and the highest thermal lift is 0.998 for both cyclohexane/DMSO and water/furfural. An increase of the temperature lift gives decreasing values for thermal yield. Furthermore, the large difference of their boiling point also shows the variations of the compositions as it boils off at a constant temperature at that certain composition. The three mixtures are found to be azeotrope mixtures and behave differently according to a certain temperature at a certain composition hence hard to separate.

The influence of the molar ratio, molar enthalpy, and molar fractions are greatly studied and has significant results to the temperature lift. The behavior of absorbent and refrigerant are also demonstrated and it is important to remember that the molar enthalpy, mole fractions, molar flows of the absorbent strongly affects the temperature lift. To add, the temperature lift gradually increases when the demixing temperature increases and lastly, the hotter the temperature of T_{P1} the better the temperature lift.

4.1.2 RECOMMENDATIONS

The feasibility of changing the distillation column by an absorber has been studied but it is also important to further study the influence of the number of theoretical stages and the height of the absorber to the temperature lift. Furthermore, the use of more than one heat exchanger to better performance can be also taken into account.

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6.0 <u>APPENDIX</u>

1. Aspen HYSY used to determine the values of the parameters:

   a) Furfural/Water Mixture
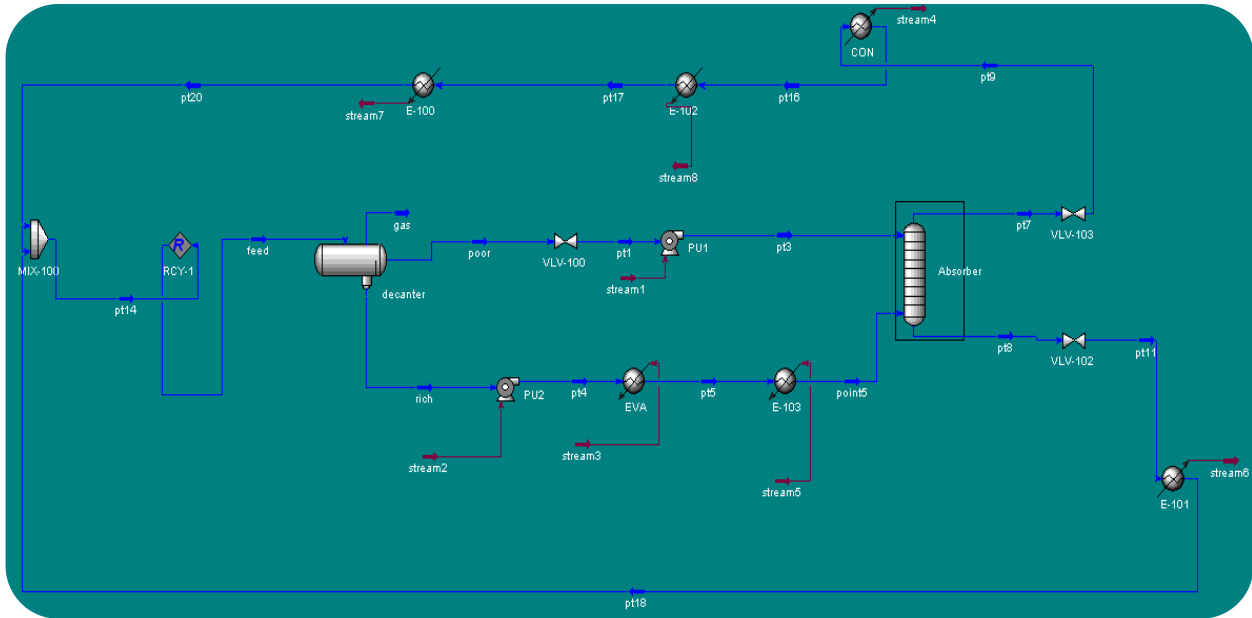
3 Phase Separator: decanter

Worksheet	Name	feed	poor	gas	rich
Conditions	Vapour	0.0000	0.0000	1.0000	0.0000
Properties	Temperature [C]	69.94	69.94	69.94	69.94
Composition	Pressure [kPa]	89.00	89.00	89.00	89.00
PF Specs	Molar Flow [kgmole/h]	100.0	78.55	0.0000	21.45
	Mass Flow [kg/h]	5705	5289	0.0000	416.3
	Std Ideal Liq Vol Flow [m3/h]	5.066	4.654	0.0000	0.4122
	Molar Enthalpy [kJ/kgmole]	-2.390e+005	-2.279e+005	-2.316e+005	-2.800e+005
	Molar Entropy [kJ/kgmole-C]	83.52	100.8	154.7	20.18
	Heat Flow [kJ/h]	-2.390e+007	-1.790e+007	0.0000	-6.004e+006

3 Phase Separator: decanter

Worksheet		feed	poor	gas	rich
Conditions	H2O	0.5000	0.3684	0.9161	0.9821
Properties	Furfural	0.5000	0.6316	0.0839	0.0179
Composition	n-Heptane	0.0000	0.0000	0.0000	0.0000
PF Specs	Cyclohexane	0.0000	0.0000	0.0000	0.0000
	diMSulfoxide	0.0000	0.0000	0.0000	0.0000
	DMF	0.0000	0.0000	0.0000	0.0000

b) N-heptane/DMF

3 Phase Separator: decanter

Worksheet		feed	poor	gas	rich
Conditions	H2O	0.0000	0.0000	0.0000	0.0000
	Furfural	0.0000	0.0000	0.0000	0.0000
Properties	n-Heptane	0.1270	0.1269	0.2993	0.1269
	Cyclohexane	0.0000	0.0000	0.0000	0.0000
Composition	diMSulfoxide	0.0000	0.0000	0.0000	0.0000
PF Specs	DMF	0.8730	0.8731	0.7007	0.8731

Heater: EVA

Worksheet	Name	pt4	pt5	stream3
Conditions	Vapour	0.0000	1.0000	<empty>
	Temperature [C]	195.0	300.0	<empty>
Properties	Pressure [kPa]	360.1	360.2	<empty>
	Molar Flow [kgmole/h]	0.0000	0.0000	<empty>
Composition	Mass Flow [kg/h]	0.0000	0.0000	<empty>
	Std Ideal Liq Vol Flow [m3/h]	0.0000	0.0000	<empty>
PF Specs	Molar Enthalpy [kJ/kgmole]	-2.051e+005	-1.531e+005	<empty>
	Molar Entropy [kJ/kgmole-C]	216.0	302.5	<empty>
	Heat Flow [kJ/h]	0.0000	0.0000	0.0000

Column: Absorber / COL1 Fluid Pkg: Basis-1 / UNIQUAC - Ideal

Design

Connections
Monitor
Specs
Specs Summary
Subcooling
Notes

Column Name: Absorber   Sub-Flowsheet Tag: COL1

Ovhd Vapour Outlet: pt7

Top Stage Inlet: pt3

Optional Inlet Streams

Stream	Inlet Stage
<< Stream >>	

Bottom Stage Inlet: point5

Stage Numbering
⦿ Top Down   ○ Bottom Up
Edit Trays...

1
2
Num of Stages
n = 25
n-1
n

P1 350.3 kPa

Pn 352.0 kPa

Optional Side Draws

Stream	Type	Draw Stage
<< Stream >>		

Bottoms Liquid Outlet: pt8

Design | Parameters | Side Ops | Rating | Worksheet | Performance | Flowsheet | Reactions | Dynamics

Delete | Column Environment... | Run | Reset | Converged | ☑ Update Outlets ☐ Ignored

35

c) Cyclohexane/DMSO