# THE REMOVAL OF IMPURITIES FROM A PROCESS STREAM.

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# THE REMOVAL OF IMPURITIES FROM A PROCESS STREAM.

by

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# DECLARATION

I hereby certify that this thesis is my own original work, except for the acknowledgements in the text.

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# ABSTRACT

The high purity 1-octene produced by Sasol Alpha Olefins in Secunda and which is sold to DOW Chemical Company for co-monomer application, has performed poorly over the DOW Ziegler-Natta catalysts. The reason for the poor performance was catalyst poisoning caused by low-level impurities present in the 1-octene. Much work from Sasol and DOW has gone into identifying the components responsible for catalyst deactivation, as well as methods suitable for removing them without significant 1-octene losses.

Super NMP (n-Methyl-2-Pyrrolidone) extractive distillation piloting was performed previously on 1-octene in order to remove the low-level impurities that deactivate the DOW catalysts.

VLE (vapour liquid equilibrium) test work performed previously indicated that all xylenol isomers are more promising as extractive distillation solvents than NMP.

The aim of this project was to perform extractive distillation using NMP, xylenol and a mixture of NMP and xylenol (1:1), as extraction solvents, on the same feed material (pre-guarded 1-octene feed). The results were compared and the performance of the solvents was evaluated. The best solvent was selected from the performance-evaluation and the process conditions were optimised.

If xylenol or the NMP/xylenol mixture proved to be more promising as an extractive distillation solvent than NMP, extensive research would be required to determine the impact on the current octene plant in Secunda.

An Aspen Plus simulation model was also generated and the predictions of the model were compared to the data obtained from the pilot plant test work. The accuracy of the model was verified over a wide range of conditions. The

Aspen Plus model was also used to identify operational problems and process uncertainties.

From the pilot plant test work, xylenol proved to be more promising as an extraction solvent than NMP and the NMP/xylenol mixture (1:1). However, the NMP/xylenol mixture (1:1) proved more efficient than NMP.

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# CONTENTS

# CHAPTER 1

# INTRODUCTION

At the end of 1996 Sasol Technology initiated a project for the purification of 1-octene from the hydrocarbon material produced in the Synthol reactors, at the Sasol Secunda plant. The plant was to process overhead material from the Synthol Light Oil (SLO) splitter columns and form part of the Alpha Olefins production facility. Linde A.G. became involved in the development of the process in early 1997 and the plant was successfully commissioned in early 1999. The 1-octene purification process that was developed for the first plant consisted of the following steps:

- Acid removal step
- Prefractionation to produce a C8 broad-cut
- Oxygenate removal in an extractive distillation system using NMP as a solvent
- Superfractionation

DOW Chemical Company uses the Sasol 1-octene for co-monomer application. DOW has reported that the Sasol 1-octene deactivates the Ziegler-Natta catalysts, which is used in their process.

Super NMP extractive distillation piloting was performed on the high purity 1-octene in order to remove the low-level impurities. Six samples were prepared in November/December 2000 in an attempt to evaluate the effect of pressure, solvent-to-feed-ratio and reflux-ratio, on the efficiency of impurity removal from Sasol 1-octene. These samples were prepared using post-guardbed 1-octene.

As the super extractive distillation step fits ideally into the Secunda 1-octene train, prior to guardbedding, further tests were conducted under different conditions to those used for the first six samples. The effect of the guardbed treatment was also investigated by alternating between pre- and post-guardbed feed. These tests were performed during March 2001.

An additional set of runs were performed during June 2001 in order to produce a final sample for DOW Chemical Company, to confirm the success of the super NMP extractive distillation for the removal of the low-level impurities. During these runs, the effect of the ratio of the internal reflux and external reflux was also evaluated as well as the influence of lower solvent-to-feed-ratios.

The November/December 2000-samples performed poorly over the DOW catalyst due to the presence of 5 – 12 ppm NMP in the sample, following lights removal and a standard guardbed treatment.

However, when these samples were extensively treated in the guardbed, the DOW catalyst activity increased to 100% due to the complete removal of the solvent.

As a result, it was ensured that the samples produced during June 2001 did not contain any NMP in the overheads. This was achieved by increasing the packed height of the stripping section in the distillation column. Results from these runs indicated that the best operating condition for super extractive distillation relies on an optimisation between reflux and solvent-to-feed-ratio. The reflux can be controlled by varying the solvent feed-temperature, which in turn affects the solvent-to-feed-ratio. An increase in the solvent feed-temperature results in a decrease in internal 1-octene traffic and a higher effective solvent-to-feed-ratio.

Prof. Nieuwoudt from University of Stellenbosch performed test work on NMP in order to improve the extraction qualities of NMP. Solvents were sought that could be added to NMP to improve the separation in the extractive distillation column.

A theoretical study was conducted to develop solvents with the potential to decrease the volatility of the impurities present in the 1-octene. Solvents, which are commercially available and have identical functionality to those predicted by the theoretical study, were used in a VLE still in order to evaluate the performance. The results were expressed as a relative volatility of 1-octene to total impurities.

**Table 1.1**

| **Solvent mixture** | **Relative volatility, $\alpha$** |
|---|---|
| Diphenylsulfoxide + NMP | 1.15 |
| 1,5-Dicyanopentane + NMP | 1.129 |
| Adiponitrile + NMP | 1.129 |
| 2,4-Xylenol + NMP | 1.107 |
| 3,4-Xylenol + NMP | 1.101 |
| 2,6-Xylenol + NMP | 1.089 |
| Mixed Xylenols + NMP | 1.067 |
| Butyl-benzene-sulfonamide + NMP | 1.065 |
| m-Cresol + NMP | 1.064 |
| 3,5-Xylenol + NMP | 1.059 |
| Benzonitrile + NMP | 1.056 |
| Diphenyl + Diphenyloxide + NMP | 1.053 |
| n-Methyl-Formanilide + NMP | 1.046 |
| Di-benzyl-sulfoxide + NMP | 1.039 |
| ***NMP (pure)*** | ***1.02*** |
| Ethyl-Toluene-sulfonamide + NMP | 1.014 |
| Di-phenyl-sulfone + NMP | 0.995 |
| NN-Dibutylformamide + NMP | 0.991 |
| Di-ethylene-glycol + NMP | 0.985 |

From the above results, it was concluded that it would be in Sasol's interest to conduct research into the possibility of using a better solvent than the existing NMP. The xylenol + NMP solvent mixture suited Sasol i.t.o. price and availability, hence this research project was initiated.

If xylenol or the NMP/xylenol mixture proved to be better in extracting the impurities from the 1-octene stream, then extensive research would be required to:

- determine the optimum operating conditions of the new solvent
- do intensive piloting in a closed loop to identify any process problems
- do a feasibility study to confirm the impact of using the new solvent on a commercial scale
- do a conceptual design on the new distillation unit

# CHAPTER 2

# LITERATURE STUDY

Extractive distillation can be considered when volatility differences between the species to be separated are so small that a very large number of trays are required in the distillation column.

In extractive distillation, a solvent is added to the distillation column in order to increase the relative volatility of the key components in the feed. Extractive distillation will normally apply in systems having low relative volatilities, or in systems which exhibit azeotropes. The effective extractive solvent will selectively interact with one (or more) of the components, thereby increasing the relative volatilities [1].

Normally, an extractive solvent is selected which boils at a much higher temperature than the components in the feed. The solvent should be selected so that no new azeotropes are formed. Other factors that has to be considered when selecting an extractive solvent is:

- Availability
- Toxicity
- Stability
- Freezing point
- Extractive power

In order to maintain a high concentration of solvent throughout the column, the solvent is normally introduced only a few trays below the top of the column (with the exact locations being determined by the necessity to reduce the solvent concentration in the overhead vapour).

The choice of solvent determines which components becomes the overhead product. Since the reflux at the top of the column dilutes the solvent, the advantage of higher reflux must be balanced against the disadvantage of a lower solvent concentration and a reduction in relative volatility.

## 2.1 Ideal vapours and liquids

The ideal gas law predicts the behaviour of an ideal gas. No real gas behaves like the ideal gas law over all ranges of temperature and pressure. This is due to the effect of intermolecular forces (molecules attract or repel each other) and the size of the molecules (the size of the molecules makes it difficult to compress a gas at high pressures) [2].

"Lighter" gases ($H_2$, $O_2$) behave like an ideal gas under normal circumstances. "Heavier" gases ($SO_2$, $C_2H_4$) deviate from the ideal gas law, especially at high pressures and low temperatures (due to intermolecular forces) [3].

In liquids, the forces of attraction are much greater than the forces in the gaseous state, as a result of the smaller distances between the molecules.

The deviation from ideal behaviour must be incorporated in distillation design calculations. The deviation from ideality can be expressed in a number of ways and are discussed below.

## 2.2 Vapour-Liquid Equilibrium (VLE)

Most distillation design methods include equilibrium as one of the boundary conditions for design calculations, hence equilibrium data must be available for such calculations.

The separation of a mixture in the distillation process is achieved by manipulating the conditions (temperature and pressure) to ensure that a vapour and liquid phase exist (at different concentrations of the materials to be separated) [2]. The composition of the vapour in equilibrium with a liquid of given composition is determined experimentally by using an equilibrium still.

The results from the equilibrium still are plotted in the form of a phase diagram. Phase diagrams are used to describe two component systems (binary systems) by plotting two out of the following three variables: composition, temperature and pressure (Fig. 2.2 A – G). The most popular of these plots is the x – y plot (Fig. 2.1, 2.2 A – C) [4].

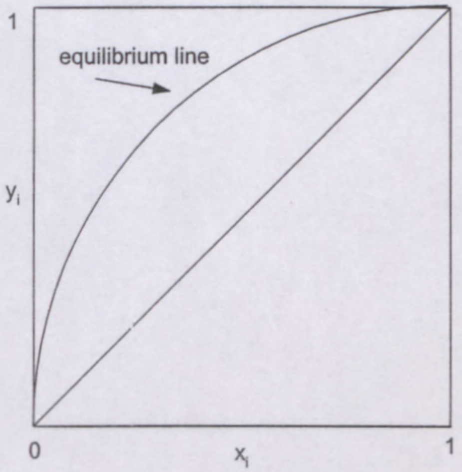


**Fig. 2.1 : x – y plot**

The horizontal line represents the liquid phase mole fraction of component i and the vertical axis represents the vapour phase mole fraction of component i. The equilibrium line indicates the vapour-liquid-equilibrium (VLE) behaviour of the component. The 45° diagonal represents points at which vapour and liquid concentrations are the same. If the equilibrium line crosses the 45° diagonal, an azeotrope will exist/be present [5].

Phase diagrams can also indicate the ease of separation between the two components. The farther the equilibrium line is from the 45° line, the easier the separation will be [5].

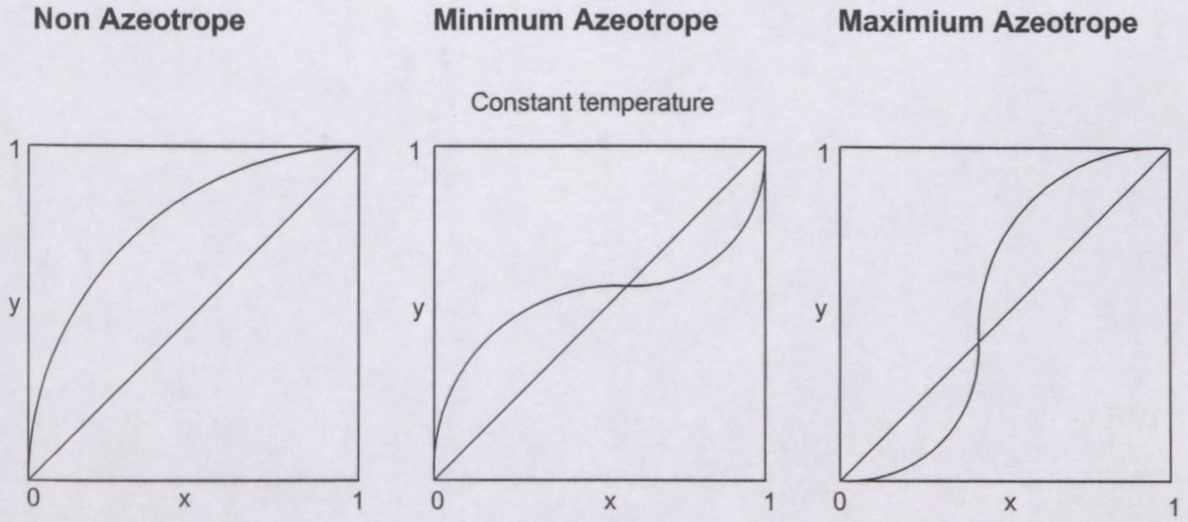


Fig. 2.2 A - C : x - y plot

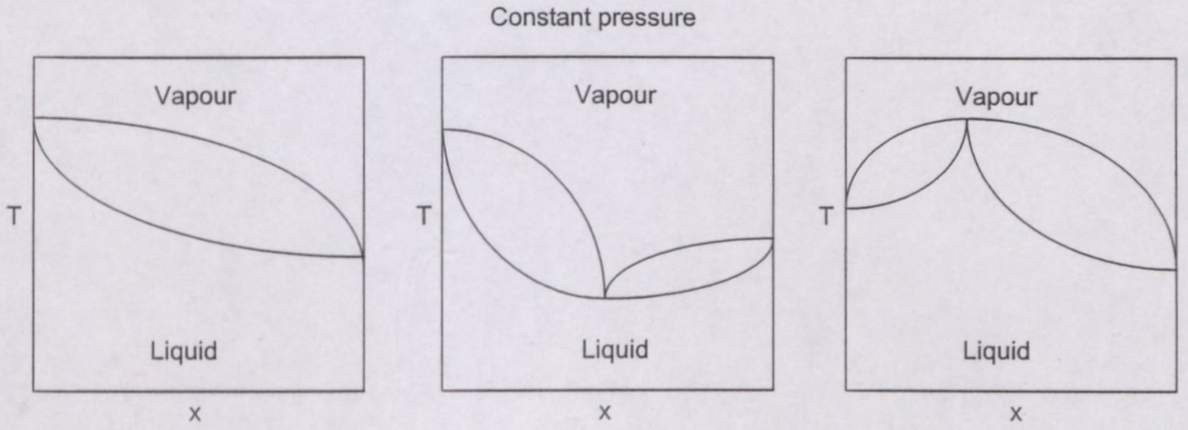


Fig. 2.2 D - F : T - x plot

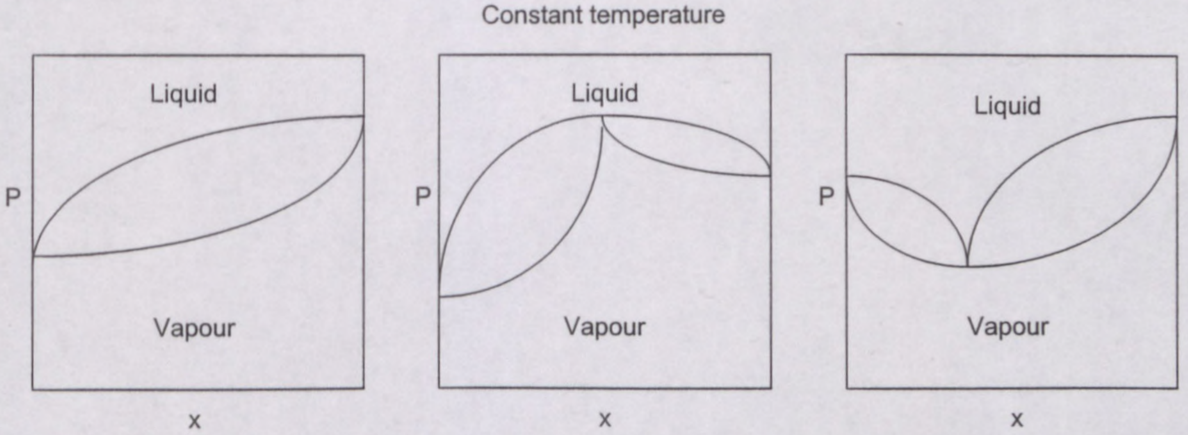


Fig. 2.2 G - I : P - x plot

The temperature-composition (T-x) diagrams (Fig. 2.2 D – F) illustrate the temperature-composition-relationship of a saturated liquid at constant pressure. Referring to Fig. 2.2 D, the bottom curve indicates the composition of the liquid, which boils at the corresponding temperature, while the top curve indicates the corresponding vapour-composition at that temperature. In Fig. 2.2 D and F there is a point where there is no change in boiling and the liquid and vapour composition is the same. This point indicates that an azeotrope is present [4]. A minimum-boiling azeotrope (Fig. 2.2 B, E, H) boils at a lower temperature than either of the pure components. During distillation, the azeotrope will report in the overhead product. A maximum-boiling azeotrope (Fig. 2.2 C, F, I) boils at a higher temperature than either of the pure components and will always report in the bottoms stream during distillation [4].

## 2.3 Ideal systems

An ideal system is one where the vapour obeys the ideal gas law and the liquid obeys Raoult's law. Raoult's law relates the partial pressure of a component in the vapour phase to its concentration in the liquid phase [2],

$$p_i = P_i.x_i \qquad (1)$$

where $p_i$ = partial pressure of component i in the vapour mixture
$P_i$ = vapour pressure of pure component i
$x_i$ = mol fraction of component i in the liquid phase

An ideal gas mixture obeys Dalton's law. Dalton's law relates the concentration of a component present in an ideal gas or vapour mixture (behaviour described by the ideal gas law), to its partial pressure [2],

$$p_i = y_i.P_t \qquad (2)$$

where $p_i$ = partial pressure of component i
$y_i$ = mol fraction of component i in gas or vapour phase

$P_t$ = total pressure

Dalton's law also states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the mixed gases [2],

$$P_t = \Sigma_1^n p_i = p_1 + p_2 + p_3 + \ldots + p_n \tag{3}$$

### 2.3.1 Relative volatility

Relative volatility is a measure of separability. As the value increases, the easier the separation [2]. Relative volatility is defined by

$$\alpha_{ij} = (y_i / x_i) / (y_j / x_j) \tag{4}$$

where $\alpha_{ij}$ = relative volatility of component i relative to component j

For an ideal mixture (e.g. octane and nonane) the relative volatility is also equal to the ratio of the pure-component-vapour-pressures of the two components,

$$\alpha_{ij} = P_i / P_j \tag{5}$$

If the relative volatility is equal to one, the vapour and liquid phases will have the same compositions. This means that it will be impossible to separate by means of distillation. The larger the relative volatility (the more it differs from one), the easier it will be to separate the two components. The following is an indication of difficulty of separation vs. relative volatility [2],

| $\alpha_{ij}$ | **Comments** |
|---|---|
| 1.00 – 1.03 | Very difficult to separate. Should not be attempted. |
| 1.05 – 1.10 | Difficult to separate, but possible. Requires super-fractionation (100 – 200 theoretical stages) |
| 1.20 – 1.50 | Fairly easy separation. (20 – 50 theoretical stages) |
| >5 | Very easy separation. Requires only a few stages. |

### 2.3.2 Equilibrium constant

At equilibrium, the concentration of any component in the liquid phase can be related to its concentration in the vapour phase by means of the equilibrium constant (K) [2].

$$K = y_i / x_I \qquad (6)$$

The equilibrium constant can be related to relative volatility by

$$\alpha_{ij} = K_i / K_j \qquad (7)$$

The vapour-liquid equilibrium composition data can be calculated for a binary system from the vapour pressure-temperature data of the pure components at atmospheric pressure [2].

## 2.4 Non-ideal systems

As mentioned before, actual gases (and mixtures) do not behave like the ideal gas law predicts. Liquids/solutions also deviate from ideality. The deviations from the ideality can be expressed in a number of ways. For distillation, the following is of importance,

### 2.4.1 Compressibility factor

$$Z = P.V / n.R.T \qquad (8)$$

where: Z is the compressibility factor expressing the ratio of the actual gas volume to that of an ideal gas at the same conditions (temperature and pressure).

The compressibility factor approaches unity at zero pressure. It also approaches unity (for most gases) at atmospheric pressure. The compressibility factor deviates at high pressures [2].

### 2.4.2 Fugacity

The fugacity coefficient is a correction factor illustrating the extent of the deviation of actual gases from ideal behaviour. The fugacity coefficient relates the partial pressure of an actual gas to that which it would exert if it behaved ideally [2],

$$\nu = f / p \qquad (9)$$

where $\nu$ = fugacity coefficient
f = fugacity
p = partial pressure

The vapour fugacity is equal to the liquid fugacity, at equilibrium [2],

$$f_v = f_l \qquad (10)$$

At lower pressures (atmospheric and below) the fugacity is equal to the partial pressure of the gas, thus

$$f_i = p_i = y_i.P_t \qquad (11)$$

The extent of ideality-deviation of components in liquid mixtures can be measured by the activity coefficient.

### 2.4.3 Activity coefficient

The activity coefficient ($\gamma$) is a correction factor relating the behaviour of actual liquids to that of ideal liquids [2]. Incorporating the correction factor to the Raoult's law,

$$p_i = \gamma_i.P_i.x_l \qquad (12)$$

If the fugacity coefficient and the activity coefficient are incorporated in equation 12, the following is obtained,

$$\nu_i . y_i . P_t = \gamma_i . P_i . x_i \qquad (13)$$

Equation 13 is used for vapour-liquid-equilibria-calculations if the variables are known or can be calculated/predicted.

The relative volatility for a non-ideal system will then be given by the following,

$$\alpha_{ij} = (y_i / x_i) / (y_j / x_j) = \gamma_i . P_i \ \nu_j / \gamma_i . P_j \ \nu_l \qquad (14)$$

The activity coefficient is an indication of how components interact in the liquid phase, i.e. an indication of how similar the components are [2].

If two components are very similar and interact ideally, the activity coefficient approximates one.

If two components are opposites in the liquid phase, they will repel each other. Activity coefficients can reach values of several thousand at infinite dilution for highly non-ideal systems [2].

When the two components have an affinity for each other, the activity coefficient can be smaller than one.

The interaction between the activity coefficients and the pure component boiling points determine whether two or more liquids will form an azeotrope at a certain composition. If a mixture of two components (with activity coefficients of greater than one) exist and the less volatile component has the higher activity coefficient, then the relative volatility between the two components will be less than expected for an ideal system [2]. If the difference in activity coefficients is large enough, the less volatile component (higher boiling point) will have the same vapour pressure as the more volatile component at a certain concentration [2]. Thus, the vapour and liquid will have the same composition. This is called the azeotropic point.

If the activity coefficients are greater than one and an azeotrope is present, the azeotrope mixture will boil at a lower temperature than either of the two pure components [2]. The azeotrope is called a low-boiling azeotrope.

If the activity coefficients are less than one and an azeotrope is present, it will result in a high-boiling azeotrope.

### 2.4.4 Non-ideal vapours and liquids

In order to obtain vapour-liquid equilibrium composition data for a binary non-ideal system, the following methods can be used [2],

1. The data can be determined experimentally.
2. The system can be assumed to be ideal and the data can be calculated from the ideal equations.
3. The data can be calculated from a few experimental points by using empirical equations.
4. The data can be estimated roughly from physical data of the pure components with the use of empirical equations.

Since no method of calculating vapour-liquid equilibrium data (for a non-ideal system) is completely accurate, actual experimental data should be used if possible [2]. If complete experimental data is not available, the third method (above) can be used. If systems are known to be approximately ideal, the use of ideal equations may be satisfactory.

## 2.5 Manipulating the relative volatility

If two compounds have a low relative volatility, it is frequently possible to increase the relative volatility by adding a solvent.

A method in identifying/selecting possible solvents is to concentrate on the activity coefficients of the two compounds at infinite dilution in the potential solvent [2].

The relative volatility of the two compounds in the presence of a solvent [2], is given by applying equation 15.

$$\alpha_{12} = \gamma^{\infty}{}_1.P^s{}_1 / \gamma^{\infty}{}_2.P^s{}_2 \qquad (15)$$

where $P^s{}_1$ , $P^s{}_2$ = saturation vapour pressure

The ratio of $\gamma^{\infty}{}_1 / \gamma^{\infty}{}_2$ composes a general selectivity factor and can be used to rate the selectivity of solvents [2]. The ratio of activity coefficients varies with composition and in most cases it reaches a maximum when the components are at infinite dilution [2]. If the ratio is close to unity at finite concentrations, the solvent is not suitable [2].

*Example:*

Consider the distillation of hexane and cyclohexane. The activity coefficients at infinite dilution (at 60°C) in the presence of NMP (n-Methyl-2-Pyrrolidone) and DMF (Dimethyl Formamide) respectively, are

| **SOLVENT** | $\gamma^4$ **hexane** | $\gamma^4$ **cyclohexane** | $\gamma^4$ **hexane /** $\gamma^4$ **cyclohexane** |
|---|---|---|---|
| NMP | 9.20 | 6.40 | 1.44 |
| DMF | 12.15 | 9.90 | 1.23 |

The above indicates that NMP will be the suitable solvent for the application, since the $\gamma^4$hexane / $\gamma^4$cyclohexane-value for NMP is greater than the $\gamma^4$hexane / $\gamma^4$cyclohexane-value for DMF [2].

# CHAPTER 3

# PILOTING : EXPERIMENTAL

The performances of the different solvents were evaluated on a pilot plant scale. A base run using each solvent was performed. Optimisation tests for the xylenol and the NMP/xylenol mixture (1:1) had to be conducted since the NMP base run was performed at already-optimised-conditions (obtained from previous piloting). From the optimised results, the best extraction solvent was selected and the conditions were optimised further.

The project was conducted in the following chronological format:

- A base run was performed using NMP as the extraction solvent (Mode 1).
- A base run was performed using xylenol as the extraction solvent (Mode 2 and 3).
- A base run was performed, using a mixture of NMP and xylenol (1:1) as the extraction solvent (Mode 4).
- The xylenol base run conditions were optimised (Modes 5 – 9) as the NMP base run was performed at already optimised conditions.
- The NMP/xylenol mixture base run conditions were optimised (Modes 10 – 12).
- The optimised results of the three extraction solvents (NMP, xylenol and NMP/xylenol mixture) were compared. From the results, the best extraction solvent was selected and the conditions were optimised (Modes 13 – 17).

The feed material and solvents used during the piloting were:

- Pre-guarded 1-octene feed
- NMP (n-Methyl-2-Pyrrolidone)
- LXHBTA (light xylenol high boiling tar acids)
- NMP/xylenol mixture of 1:1. For the purpose of this project, it was not necessary to adjust the ratio of the mixture.

## 3.1 Equipment configuration

Being the pilot plant project co-ordinator for this project, the following had to be in place before the plant could be commissioned:

1. Define experimental program and deliverables (data collection, analyses and specifications) of the project.
2. Conduct a PPA (potential problem analysis), i.e. to act pro-actively to avoid any problems (injury, pollution, process upset, etc.) that may be encountered.
3. Ensure that the configuration of the equipment is suited for the project. Also prepare the plant in terms of product compatibility, operating conditions and deliverables. A hazop study was conducted on the required modifications. The modifications were implemented and signed off.
4. Co-ordinate the feed requirements (quantity, type, containers, specification).
5. Compile a pre-commissioning checklist to ensure that everything is in place before commissioning commences, i.e. feed requirements, containers, equipment (cleanliness, pumps, instrumentation, etc.), analytical, logistics.
6. Compile start-up and operating procedures.

A multi-purpose continuous distillation pilot plant was used for the piloting. The column had the following configuration:

- 10 sections, each section packed with 1m of Rombopak 12M structured sheet metal packing, which translates to approximately 60 – 80 theoretical plates, depending on the loading of the column.
- Solvent feed between section 2 and 3, numbering from the top.
- 1-octene feed between section 7 and 8, numbering from the top.
- Pre-heater on the solvent feed stream.
- Solvent feed rate up to 30 kg/hr.
- Octene feed rate up to 2 kg/hr.
- Reflux rate up to 6 kg/hr.
- Pressure of 40 kPa absolute.
- The solvent was fed from a pressure vessel (F7353) through FIC73134.
- The 1-octene was fed from a pressure vessel through FIC73131.

- The overheads passed through FI73132 and a needle valve and was collected in a 200lt drum (standing on a scale).
- The bottoms passed through J7386 and FIC73001 and was collected in a milk-can.

The Piping- and Instrumentation diagram (P&ID) of the plant is attached (Fig. 3.1).

## 3.2 Pilot plant design

A multi-purpose distillation pilot plant was used for the piloting – MCD110. The plant is considered as a multi-purpose column in that it can be operated at full vacuum and a maximum pressure of 15 bar and is equipped with two feed systems.

The column has an internal diameter of 110mm and it is equipped with 10m of Rombopak 12M structured packing (10 sections, each packed with 1m of packing). The column is also equipped with internals, i.e. collectors and distributors. Calibration tests confirmed that the total packed height equates to 80 theoretical stages. The calibration of the packing was done at 80% loading from the flood point.

The column consists of 10 sections, each measuring 1.1m in length. Each section is fitted with the following equipment:

- A thermocouple measuring the vapour temperature
- One liquid feed point
- One liquid sample point
- One wall heater to minimise the heatloss to the surroundings

The thermosyphon reboiler is designed for 18 kW. The reboiler can be controlled on temperature-control or power (kW) control. The temperature-control was used during this project to adjust the 1-octene recovery, which was the control parameter. The elements are protected against high temperature by means of temperature trips as well as a low-level switch in the reboiler. The reboiler is equipped with a float-type level indicator and the level is controlled by means of a control valve on the bottoms discharge line.

The column is equipped with an internal condenser as well as an external condenser. The external condenser was used during this project, as an external reflux was required. The condenser is equipped with chiller water at 5°C and is designed for a total duty of 25 kW. The temperature of the liquid leaving the condenser can also be controlled via a control valve on the chiller water line, which controls the chiller water flow through the condenser.

The column can be operated under pressure or vacuum. Vacuum is created by means of a two-stage steam ejector system. The vacuum is controlled by purging nitrogen into the system by means of a control valve. The vacuum transmitter is situated at the top of the column and the nitrogen is introduced in the reflux drum. The vacuum system is equipped with a knock-out condenser (chiller water at 5°C) to ensure that no vapours are lost through the vacuum system.

Octene-balances as well as total mass balances were done throughout the pilot plant test work and confirmed that no product was lost through the vacuum system.

The reflux drum is equipped with a phase separation plate, which allows for separation/decanting of two different phases. This plate was not used during this project, hence only the one side of the drum was used (A-side). The reflux system is also equipped with a knock-out system, which is used to drain water from the system under vacuum. The 1-octene feed material contained a small amount of water (0.27% m/m). The water did eventually build up in the knock-out system and was drained.

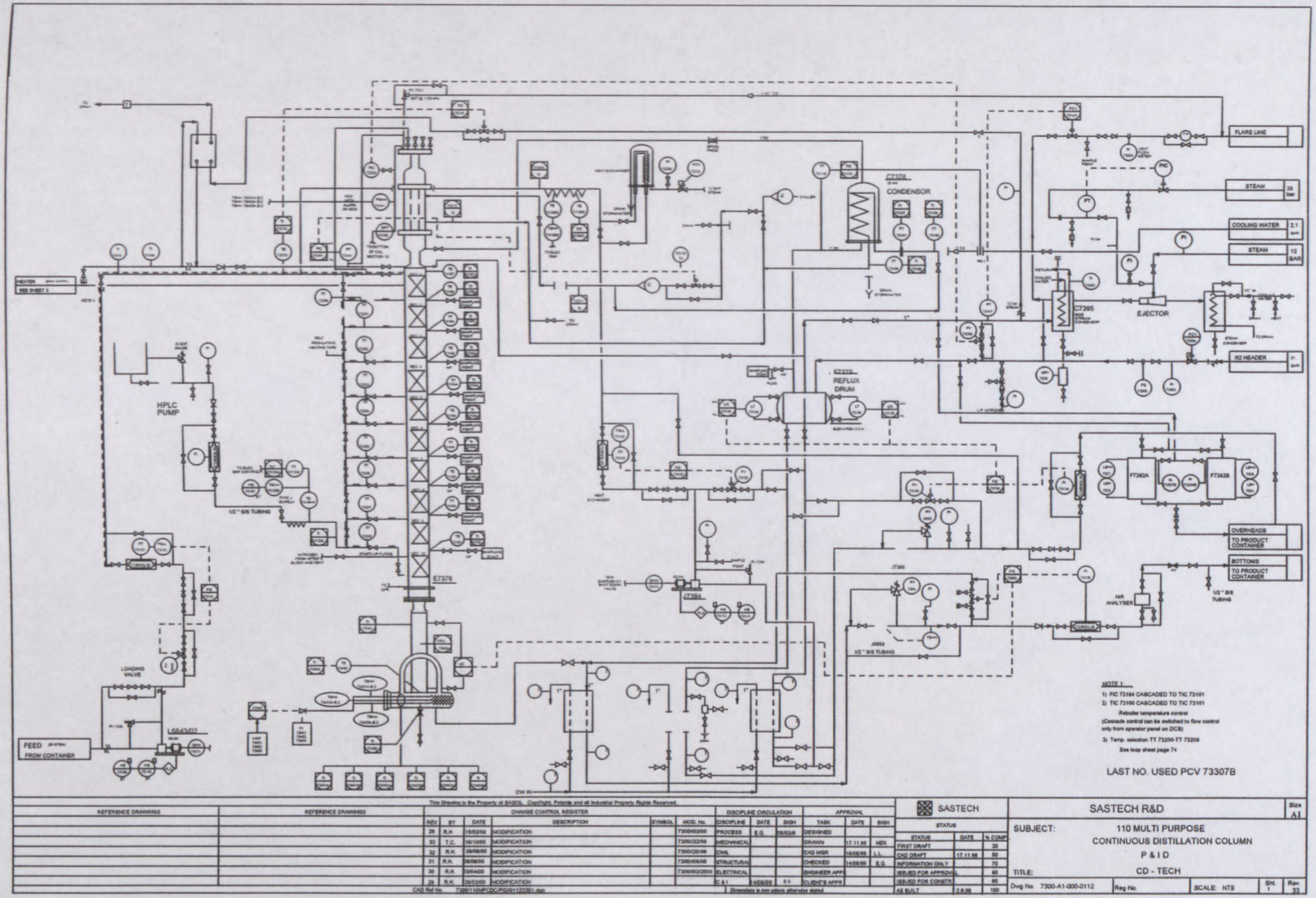


Fig. 3.1 P&ID of MCD110 pilot plant distillation column

The reflux gear pump can operate under vacuum and pressure and the flow is controlled by means of a control valve and is measured by a coriolis mass flowmeter. The overhead product is also measured by a coriolis mass flowmeter and it is controlled manually by means of a needle valve.

The reflux system is equipped with a coil steam heater, which is used if it is required that the reflux be heated before entering the column. During this project it was not required to use this unit.

The column is equipped with two feed systems. The solvent is fed from a pressure vessel (F7353) through a flow control valve to the column. Flow is established by means of differential pressure. From experience, the reliability of a system is very dependant on pumps. By eliminating a pump from the system, the reliability is increased. The same philosophy was used in the second feed system. The 1-octene was fed from an intermediate-bulk-container with the flow created by means of differential pressure and controlled via a control valve.

The solvent is pre-heated by means of a plate heat exchanger. Steam-flow is controlled through the heat exchanger by means of a control valve. The 1-octene feed was not pre-heated.

## 3.3 Pilot plant operation

During this project the extractive distillation column had to be commissioned and de-commissioned several times between the different modes/stages that used different solvents. Between modes that used different solvents, the column had to be cleaned by means of steam.

While commissioning the extractive distillation column, contamination of the overheads system with the solvent must be avoided. If the overheads system is contaminated with solvent, the system must be drained to a minimum and the reflux flow must be increased until the solvent has been washed from the overheads product. On this pilot plant scale, such a process upset can cause a production loss of up to 36 hours. During this project the solvent-content in the overheads was not a critical control parameter. The data was normalised to a 0% solvent content.

In order to prevent solvent-contamination in the overheads system, the extractive distillation column was brought into operation as follows:

- The reboiler was filled to a level of 40% with the solvent.
- The reboiler level was increased to ± 55% with 1-octene.
- The reboiler elements were switched on and the vacuum was introduced to the system.
- The section wall heaters were brought into operation at this point as to minimise the heat loss to the surroundings.
- The temperature profile increased in the column as energy was introduced via the reboiler elements. When the temperature profile was just below the solvent feed point (between section 2 & 3) the solvent feed was introduced at the required flow and temperature. The 1-octene feed was also introduced at the required flow at this time.
- The reboiler level was maintained at 55% (below the vapour inlet of the thermosyphon and above the LSLL-switch).
- When the level in the reflux drum (A-side) reached ± 20%, the reflux system was commissioned at a flow of ± 2 kg/hr. The reflux flow was adjusted to maintain a steady level in the reflux drum, and increased to the required flow. It is essential that the vacuum had to be reduced (to about 70 kPa abs) before the reflux pump was brought into operation. The reason for this was to ensure that the pump had maximum suction and that it could not cavitate.
- From the point of starting the solvent feed, the reflux system was checked for water every two hours, by draining the water knock-out system.
- Commenced with taking off overheads and bottoms at the required flows.
- Commenced with analysing the bottoms (to determine the recovery of 1-octene) and the overheads (to determine the purity of 1-octene).

## 3.4 Pilot plant conditions

### 3.4.1 MODE 1 (NMP base run)

The run was conducted at optimised conditions (obtained from previous piloting on the 4" catalytic distillation pilot plant) and are indicated below. The required recovery of 1-octene was aimed at 75 - 80%.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 80°C |
| Re-boiler temperature (TI73100) | 151.5°C |
| Top temperature (TI 73107) | 89.86°C |
| Reflux rate | 2 kg/h |
| Distillate | 0.7 kg/h |
| Bottoms | 25.3 kg/h |
| Average bottoms 1-octene content | 0.94% |
| 1-octene recovery | 75.78% |
| Duty | 4.78 kW |

### 3.4.2 MODE 2 (Xylenol base run)

The xylenol base run was conducted at the same conditions as the NMP base run. The required recovery of 1-octene was aimed at 75 – 80%.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 113°C |
| Re-boiler temperature (TI 73100) | 149.74°C |
| Top temperature (TI 73107) | 87.69°C |
| Reflux rate | 2 kg/h |
| Distillate | 0.7 kg/h |
| Bottoms | 25.3 kg/h |
| Average bottoms 1-octene content | 1.31% |
| 1-octene recovery | 66.25% |
| Duty | 4.02 kW |

### 3.4.3 MODE 3 (Xylenol base run)

The second xylenol base run was conducted at the same conditions as the first xylenol base run (MODE 2), except that the reflux rate was increased to 4 kg/h (reflux : feed ratio increased from 2 :1 to 4 : 1). The required recovery of 1-octene was aimed at 70%.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 113°C |
| Re-boiler temperature (TI 73100) | 152.63°C |
| Top temperature (TI 73107) | 90.73°C |
| Reflux rate | 4 kg/h |
| Distillate | 0.7 kg/h |
| Bottoms | 25.3 kg/h |
| Average bottoms 1-octene content | 1.19% |
| 1-octene recovery | 69.34% |
| Duty | 4.02 kW |

### 3.4.4 MODE 4 (NMP/xylenol (1:1) base run)

The NMP/xylenol (1:1) mixture base run was conducted at the same conditions as the NMP base run. The required recovery of 1-octene was aimed at 75%.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 96.5°C |
| Re-boiler temperature (TI 73100) | 177.93°C |
| Top temperature (TI 73107) | 87.1°C |
| Reflux rate | 2 kg/h |
| Distillate | 0.7 kg/h |
| Bottoms | 25.3 kg/h |
| Average bottoms 1-octene content | 0.98% |
| 1-octene recovery | 74.75% |
| Duty | 5.14 kW |

### 3.4.5 MODE 5 (Xylenol optimisation run)

The next series of runs (MODES 5 – 9) were aimed to optimise the xylenol conditions. The parameters that were changed, were:

- the solvent feed temperature
- the 1-octene recovery
- the solvent : feed ratio

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 125°C |
| Re-boiler temperature (TI 73100) | 165.76°C |
| Top temperature (TI 73107) | 89.5°C |
| Reflux rate | 2 kg/h |
| Distillate | 0.8 kg/h |
| Bottoms | 25.2 kg/h |
| Average bottoms 1-octene content | 0.78% |
| 1-octene recovery | 79.93% |
| Duty | 4.01 kW |

### 3.4.6 MODE 6 (Xylenol optimisation run)

The next xylenol optimisation run was conducted at the same conditions as for MODE 5, but at a lower recovery, i.e. ±70%.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 125°C |
| Re-boiler temperature (TI 73100) | 162.89°C |
| Top temperature (TI 73107) | 89.41°C |
| Reflux rate | 2 kg/h |
| Distillate | 0.8 kg/h |
| Bottoms | 25.2 kg/h |
| Average bottoms 1-octene content | 1.09% |
| 1-octene recovery | 71.96% |
| Duty | 4.36 kW |

### 3.4.7 MODE 7 (Xylenol optimisation run)

The next xylenol optimisation run was conducted at a 75% recovery and a lower solvent feed temperature, i.e. 100°C.

| **Parameter** | **Value** |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 100°C |
| Re-boiler temperature (TI73100) | 162.85ºC |
| Top temperature (TI73107) | 89.5ºC |
| Reflux rate | 2 kg/h |
| Distillate | 0.8 kg/h |
| Bottoms | 25.2 kg/h |
| Average bottoms 1-octene content | 0.96% |
| 1-octene recovery | 75.3% |
| Duty | 4.66 kW |

### 3.4.8 MODE 8 (Xylenol optimisation run)

The next xylenol optimisation run was run at a higher recovery, i.e. ±90%.

| **Parameter** | **Value** |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 100°C |
| Re-boiler temperature (TI 73100) | 164.01ºC |
| Top temperature (TI 73107) | 89.65ºC |
| Reflux rate | 2 kg/h |
| Distillate | 0.8 kg/h |
| Bottoms | 25.2 kg/h |
| Average bottoms 1-octene content | 0.47% |
| 1-octene recovery | 87.91% |
| Duty | 4.87 kW |

### 3.4.9 MODE 9 (Xylenol optimisation run)

The final xylenol optimisation run of this series was run at a 75% 1-octene recovery, a solvent feed temperature of 125°C and a solvent : feed ratio = 15 : 1.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 2 kg/h |
| Feed (solvent) | 30 kg/h |
| Solvent temperature | 125°C |
| Re-boiler temperature (TI 73100) | 158.37°C |
| Top temperature (TI 73107) | 90.51°C |
| Reflux rate | 4 kg/h |
| Distillate | 1.5 kg/h |
| Bottoms | 30.5 kg/h |
| Average bottoms 1-octene content | 1.62% |
| 1-octene recovery | 74.78% |
| Duty | 4.8 kW |

### 3.4.10 MODE 10 (NMP/xylenol (1:1) optimisation run)

The next series of runs (MODES 10 - 12) were aimed to optimise the NMP/xylenol conditions. The solvent feed temperature was adjusted as well as the reflux : feed ratio. The 1-octene recovery was aimed at 75% for all three runs.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 79°C |
| Re-boiler temperature (TI 73100) | 170.51°C |
| Top temperature (TI 73107) | 88.45°C |
| Reflux rate | 2 kg/h |
| Distillate | 0.7 kg/h |
| Bottoms | 25.3 kg/h |
| 1-octene recovery | 72.36% |
| Average bottoms 1-octene content | 1.07% |
| Duty | 4.54 kW |

### 3.4.11 MODE 11 (NMP/xylenol (1:1) optimisation run)

The solvent feed temperature was increased to 85°C.

| **Parameter** | **Value** |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 85°C |
| Re-boiler temperature (TI 73100) | 176.77ºC |
| Top temperature (TI 73107) | 88.65ºC |
| Reflux rate | 2 kg/h |
| Distillate | 0.7 kg/h |
| Bottoms | 25.3 kg/h |
| Average bottoms 1-octene content | 0.98% |
| 1-octene recovery | 74.69% |
| Duty | 4.57 kW |

### 3.4.12 MODE 12 (NMP/xylenol (1:1) optimisation run)

The reflux : feed ratio was increased from 2 : 1 to 4 : 1. The solvent feed temperature increased to 94°C as well.

| **Parameter** | **Value** |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 1 kg/h |
| Feed (solvent) | 25 kg/h |
| Solvent temperature | 94°C |
| Re-boiler temperature (TI 73100) | 176.1C |
| Top temperature (TI 73107) | 88.2°C |
| Reflux rate | 4 kg/h |
| Distillate | 0.7 kg/h |
| Bottoms | 25.3 kg/h |
| Average bottoms 1-octene content | 0.99% |
| 1-octene recovery | 74.43% |
| Duty | 4.49 kW |

### 3.4.13 MODE 13 (Xylenol optimisation run)

The results obtained from the optimised conditions, indicated that xylenol performed better than NMP as well as the NMP/xylenol mixture (1:1). The next set of runs (MODE 13 – 17) were conducted to try and optimise the conditions even further. From the previous optimised conditions it was also clear that the solvent : feed ratio of 15 : 1 produced better results. It was decided to optimise at that solvent : feed ratio. The following parameters were changed:

- solvent feed temperature
- reflux : feed ratio

The 1-octene recovery was maintained between 85 and 90% for all of the runs.

| **Parameter** | **Value** |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 2 kg/h |
| Feed (solvent) | 30 kg/h |
| Solvent temperature | 125°C |
| Re-boiler temperature (TI 73100) | 161.1C |
| Top temperature (TI 73107) | 89.44°C |
| Reflux rate | 4 kg/h |
| Distillate | 1.5 kg/h |
| Bottoms | 30.5 kg/h |
| Average bottoms 1-octene content | 0.77% |
| 1-octene recovery | 88.01% |
| Duty | 4.4 kW |

### 3.4.14 MODE 14 (Xylenol optimisation run)

The reflux : feed ratio was decreased from 2 : 1 to 1 : 1.

| **Parameter** | **Value** |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 2 kg/h |
| Feed (solvent) | 30 kg/h |
| Solvent temperature | 125°C |
| Re-boiler temperature (TI 73100) | 160.4C |
| Top temperature (TI 73107) | 89.05°C |
| Reflux rate | 2 kg/h |
| Distillate | 1.5 kg/h |
| Bottoms | 30.5 kg/h |

| Parameter | Value |
|---|---|
| Average bottoms 1-octene content | 0.88% |
| 1-octene recovery | 86.3% |
| Duty | 3.96 kW |

### 3.4.15 MODE 15 (Xylenol optimisation run)

The reflux : feed ratio was increased from 1 : 1 to 3 : 1.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 2 kg/h |
| Feed (solvent) | 30 kg/h |
| Solvent temperature | 125°C |
| Re-boiler temperature (TI 73100) | 161.1°C |
| Top temperature (TI 73107) | 89.86°C |
| Reflux rate | 6 kg/h |
| Distillate | 1.5 kg/h |
| Bottoms | 30.5 kg/h |
| Average bottoms 1-octene content | 0.87% |
| 1-octene recovery | 86.45% |
| Duty | 4.47 kW |

### 3.4.16 MODE 16 (Xylenol optimisation run)

The solvent feed temperature was increased to 132°C to evaluate the reduction in internal reflux in the column.

| Parameter | Value |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 2 kg/h |
| Feed (solvent) | 30 kg/h |
| Solvent temperature | 132°C |
| Re-boiler temperature (TI 73100) | 162.37°C |
| Top temperature (TI 73107) | 89.98°C |
| Reflux rate | 6 kg/h |
| Distillate | 1.5 kg/h |
| Bottoms | 30.5 kg/h |
| Average bottoms 1-octene content | 0.71% |
| 1-octene recovery | 88.95% |
| Duty | 4.28 kW |

### 3.4.17 MODE 17 (Xylenol optimisation run)

The solvent feed temperature was increased further to 140°C to evaluate the reduction in internal reflux in the column.

| **Parameter** | **Value** |
|---|---|
| Pressure | 40 kPa abs |
| Feed (1-octene) | 2 kg/h |
| Feed (solvent) | 30 kg/h |
| Solvent temperature | 140°C |
| Re-boiler temperature (TI 73100) | 160.03°C |
| Top temperature (TI 73107) | 89.84°C |
| Reflux rate | 6 kg/h |
| Distillate | 1.5 kg/h |
| Bottoms | 30.5 kg/h |
| Average bottoms 1-octene content | 1.02% |
| 1-octene recovery | 85.21% |
| Duty | 4.46 kW |

## APPENDIX 1 : Summary of the pilot plant conditions at the different modes.

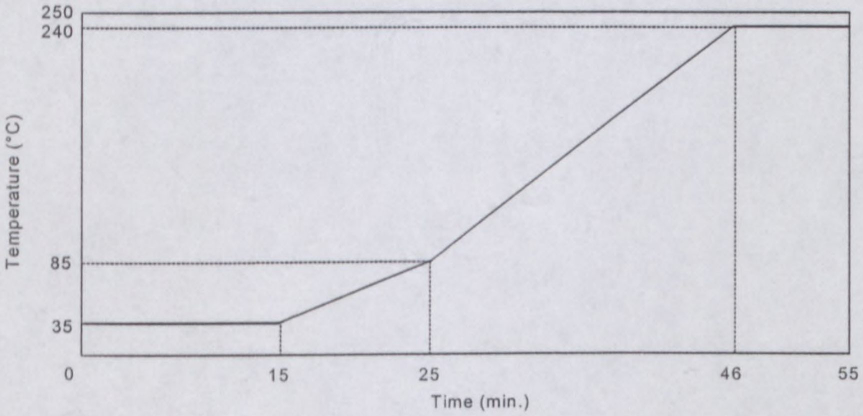
| | Date and Time | Feed 1 (98.20%) or Feed 2 (97.95%) | Solvent used | 1-octene feed rate, kg/h | Solvent feed rate, kg/h | Reflux rate, kg/h | Distillate rate, kg/h | Bottoms rate, kg/h | Solvent feed T, °C | Reboiler T, °C | Top T, °C | Average bottoms 1-octene content, % | 1-octene recovery, % | Duty, kW |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Mode 1** | 15-16/09/01, 22:00 - 21:00 | 1 | NMP | 1 | 25 | 2 | 0.7 | 25.3 | 80 | 151.5 | 89.86 | 0.94 | 75.78 | 4.78 |
| **Mode 2** | 6-7/09/01, 06:00 - 09:15 | 1 | XYLENOL | 1 | 25 | 2 | 0.7 | 25.3 | 113 | 149.74 | 87.69 | 1.31 | 66.25 | 4.02 |
| **Mode 3** | 27-28/08/01, 06:00 - 06:00 | 1 | XYLENOL | 1 | 25 | 4 | 0.7 | 25.3 | 113 | 152.63 | 90.73 | 1.19 | 69.34 | 4.02 |
| **Mode 4** | 21-22/09/01, 03:00 - 00:00 | 1 | NMP / XYLENOL | 1 | 25 | 2 | 0.7 | 25.3 | 96.5 | 177.93 | 87.1 | 0.98 | 74.75 | 5.14 |
| **Mode 5** | 05/10/01, 09:00 - 17:00 | 2 | XYLENOL | 1 | 25 | 2 | 0.8 | 25.2 | 125 | 165.76 | 89.5 | 0.78 | 79.93 | 4.01 |
| **Mode 6** | 06/10/01, 02:00 - 10:00 | 2 | XYLENOL | 1 | 25 | 2 | 0.8 | 25.2 | 125 | 162.89 | 89.41 | 1.09 | 71.96 | 4.36 |
| **Mode 7** | 06/10/01, 16:00 - 00:00 | 2 | XYLENOL | 1 | 25 | 2 | 0.8 | 25.2 | 100 | 162.85 | 89.5 | 0.96 | 75.3 | 4.66 |
| **Mode 8** | 7/10/01, 06:00 - 14:00 | 2 | XYLENOL | 1 | 25 | 2 | 0.8 | 25.2 | 100 | 164.01 | 89.65 | 0.47 | 87.91 | 4.87 |
| **Mode 9** | 9/10/01, 01:00 - 09:00 | 2 | XYLENOL | 2 | 30 | 4 | 1.5 | 30.5 | 125 | 158.37 | 90.51 | 1.62 | 74.78 | 4.8 |
| **Mode 10** | 10/11/01, 06:00 - 13:00 | 2 | NMP / XYLENOL | 1 | 25 | 2 | 0.7 | 25.3 | 79 | 170.51 | 88.45 | 1.07 | 72.36 | 4.54 |
| **Mode 11** | 10-11/11/01, 18:00 - 03:00 | 2 | NMP / XYLENOL | 1 | 25 | 2 | 0.7 | 25.3 | 85 | 176.77 | 88.65 | 0.98 | 74.69 | 4.57 |
| **Mode 12** | 13/11/01, 05:00 - 10:00 | 2 | NMP / XYLENOL | 1 | 25 | 4 | 0.7 | 25.3 | 94 | 176.1 | 88.2 | 0.99 | 74.43 | 4.49 |
| **Mode 13** | 21/11/01, 12:00 - 17:00 | 2 | XYLENOL | 2 | 30 | 4 | 1.5 | 30.5 | 125 | 161.1 | 89.44 | 0.77 | 88.01 | 4.4 |
| **Mode 14** | 22-23/11/01, 21:00 - 03:00 | 2 | XYLENOL | 2 | 30 | 2 | 1.5 | 30.5 | 125 | 160.4 | 89.05 | 0.88 | 86.3 | 3.96 |
| **Mode 15** | 23-24/11/01, 21:00 - 02:00 | 2 | XYLENOL | 2 | 30 | 6 | 1.5 | 30.5 | 125 | 161.1 | 89.86 | 0.87 | 86.45 | 4.47 |
| **Mode 16** | 24/11/01, 09:00 - 14:00 | 2 | XYLENOL | 2 | 30 | 6 | 1.5 | 30.5 | 132 | 162.37 | 89.98 | 0.71 | 88.95 | 4.28 |
| **Mode 17** | 25-28/11/01, 18:00 - 10:00 | 2 | XYLENOL | 2 | 30 | 6 | 1.5 | 30.5 | 140 | 160.03 | 89.84 | 1.02 | 85.21 | 4.46 |

## 3.5 ANALYSES and DATA LOGGING

GC analyses and column condition logging were performed as follows:

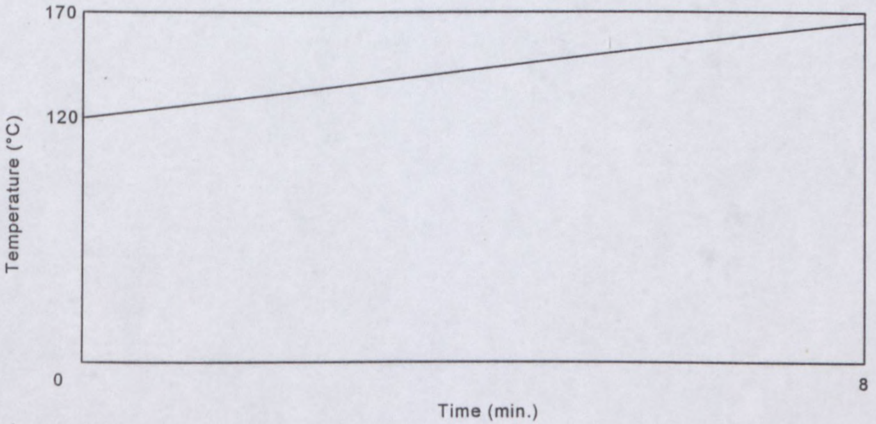
- Hourly bottoms analysis to check the bottoms 1-octene concentration.
- Two-hourly overheads analysis to monitor 1-octene purity and to establish whether solvent contamination occurred.
- Hourly logging of column temperatures, pressure, reflux and re-boiler levels, feed and product mass flows and re-boiler duty.
- The totalisers on the mass flow meters were zeroed at 06:00 daily in order to ensure accurate logistics of the feed material and product.

Overheads GC analyses were done on a DB Wax separation column (60m x 0.25m) to monitor 1-octene purity in the overheads. The GC programme is indicated below.



| Ramp | °C/min | Next °C | Hold min |
|---|---|---|---|
| Initial | - | 35 | 15 |
| Ramp 1 | 5 | 85 | 0 |
| Ramp 2 | 7.5 | 240 | 9.33 |

Bottoms GC analyses were done on a PONA separation column (60m x 0.25m) to monitor 1-octene content in the bottoms. The GC programme is indicated below.



| Ramp | °C/min | Next °C | Hold min |
|---|---|---|---|
| Initial | - | 120 | 0 |
| Ramp 1 | 5 | 160 | 0 |

Mass balances were performed during stable and on-specification operation to monitor the overall mass balance of the system.

# CHAPTER 4

# PILOTING : RESULTS

Two 1-octene feed batches were used during this project: Feed 1 and Feed 2. The two feed batches differ slightly in composition: Feed 1 (98.20% 1-octene) & Feed 2 (97.95% 1-octene). Refer to Table 4a & b for further details.

The first batch of 1-octene was used for the commissioning of the column (experienced instrumentation-, mechanical- and process-problems) and for modes 1 - 4. The second batch of 1-octene feed was used to complete the optimisation tests.

Tables 4a – d illustrate the performance measure of extractive distillation in terms of % remaining for each component, based on the specific feed used (Feed 1 or Feed 2) for the specific mode/run.

Table 4a (base run comparison), 4b (xylenol optimisation results), 4c (NMP/xylenol optimisation results) and 4d (best solvent optimisation results) indicates the GC trace results for the composite overhead products of modes 1 – 17. A comparison between these results gives a good indication of the extraction power achieved at each mode condition and helps in understanding how the different process conditions affects the extraction performance.

To illustrate the performance of the solvents graphically, the concentration-profiles of the impurities and the key components were plotted and compared to the initial feed concentrations (figure 4a – g).

The concentration-profiles of all the components were also plotted against the different modes to establish which solvent had the largest influence on extraction (figure 4h).

The GC trace results contains peak numbers. The peak numbers in the trace results correspond to the following compounds:

| | |
|---|---|
| 1 | n-Octane |
| 2a | 1-Ethyl-3-methyl cyclo-pentane (c) + (t) |
| 2b+c | 1-Ethyl-2-methyl cyclo-pentane (c) + (t) |
| 3 | 4-Octene |
| 4 | 1-Octene (can also contain t-3-octene) |
| 5 | 3,3-Dimethyl-1-hexene or 2,5-Dimethyl-2-hexene or 4-Methyl-2-heptene or 5-Methyl-3-heptene / 2-Methyl-2-heptene |
| 6 | 2-Octene (t) |
| 7a | C8 cyclic alkene |
| 7 | 3-Methyl-2-heptene or 3-Ethyl-4-methyl-1-pentene |
| 7b | 2-Octene (c) |
| 8a | Tri-methyl-cyclo-pentene isomer ? |
| 8 | 2-Ethyl-3-methyl cyclo-pentene or Ethyl cyclo-pentene with a methyl group at the 3, 4 or 5 position. |
| 9 | 1-Ethylcyclohexene or Ethenyl-cyclo-hexane or Ethyl cyclo-pentene with a methyl group at the 3, 4, or 5 position. |
| 9a | C8 cyclic alkene |
| 9b | C8 cyclic alkene |
| 10 | 1,7-Octadiene |
| 11 | 2,5-Dimethyl-1,5-haxadiene / Ethyl-cyclo-hexene |
| 12 | 1,2,3-Trimethylcyclopentene (could also include 1,4-Octadiene) |
| 13 | 3-Propyl-1,4-pentadiene |
| 14 | 2-Methyl-1,5-heptadiene (2 components include 1-Ethyl-cyclohexene) |
| 15 | 2-Methyl-1,5-heptadiene / 1,6-Octadiene |
| 16 | Iso-propyl-cyclo-pentene |
| 17 | 4-Methyl-1,6-heptadiene |
| 18 | 1,6-Octadiene (c) / C8 alkyne |
| 19 | Bicyclo[2.2.1] heptane (2-Methyl-norbornane) / branched cyclic diene / C8 alkyne |

## Table 4a (Base run comparison)

| | | Mode 1 | | Mode 2 | | Mode 3 | | Mode 4 | |
|---|---|---|---|---|---|---|---|---|---|
| Peaks | Feed 1<br>SIG21010.D | 80°C NMP feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20028.D<br>Feed 1<br>75.78% Recovery | | 113°C Xylenol feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20026.D<br>Feed 1<br>66.25% Recovery | | 113°C Xylenol Feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>4 kg/hr reflux<br>40 kPa abs pressure<br>SIG20027.D<br>Feed 1<br>69.34% Recovery | | 96.5°C Xylenol/NMP T<br>25 kg/hr xylenol/NMP<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20041.D<br>Feed 1<br>74.75% Recovery | |
| | Mass % | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining |
| 1 | 0.038031 | 0.048797 | 128% | 0.053399 | 140% | 0.074149 | 195% | 0.042561 | 112% |
| 2a+b+c | 0.187261 | 0.238289 | 127% | 0.254263 | 136% | 0.280735 | 150% | 0.219491 | 117% |
| 3 | 0 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 4 | 98.201691 | 98.73102 | 101% | 99.02822 | 101% | 98.80442 | 101% | 98.84711 | 101% |
| 5 | 0.285617 | 0.258282 | 90% | 0.222481 | 78% | 0.213202 | 75% | 0.248737 | 87% |
| 6 | 0.046304 | 0.040289 | 87% | 0.03593 | 78% | 0.038338 | 83% | 0.0386 | 83% |
| 7 | 0.008531 | 0.004012 | 47% | 0.002661 | 31% | 0.004262 | 50% | 0.003842 | 45% |
| 8 | 0.041745 | 0.043759 | 105% | 0.039354 | 94% | 0.04779 | 114% | 0.039101 | 94% |
| 9 | 0.047372 | 0.050637 | 107% | 0.030493 | 64% | 0.043343 | 91% | 0.042208 | 89% |
| 10 | 0.025681 | 0.014385 | 56% | 0.006298 | 25% | 0.014697 | 57% | 0.013479 | 52% |
| 11 | 0.22003 | 0.116885 | 53% | 0.050979 | 23% | 0.080933 | 37% | 0.098843 | 45% |
| 12 | 0.484537 | 0.36354 | 75% | 0.211859 | 44% | 0.298352 | 62% | 0.296066 | 61% |
| 13 | 0.035854 | 0.009188 | 26% | 0 | 0% | 0.009238 | 26% | 0.009918 | 28% |
| 15 | 0.098306 | 0.011491 | 12% | 0.01149 | 12% | 0.026928 | 27% | 0.032164 | 33% |
| 14 | 0.143793 | 0.041204 | 29% | 0.012992 | 9% | 0.032831 | 23% | 0.038886 | 27% |
| 16 | 0.001565 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 17 | 0.011624 | 0.001889 | 16% | 0.001731 | 15% | 0.004462 | 38% | 0.004921 | 42% |
| 18 | 0.047088 | 0.00196 | 4% | 0.001807 | 4% | 0.005059 | 11% | 0.00797 | 17% |
| 19 | 0.011085 | 0 | 0% | 0 | 0% | 0.002694 | 24% | 0.001931 | 17% |
| Light Other | 0.0013 | 0.001811 | 139.3% | 0.008365 | 643% | 0 | 0% | 0.003346 | 257% |
| Heavy Other | 0.062589 | 0.010727 | 17% | 0.017163 | 27% | 0.013879 | 22% | 0.004532 | 7% |
| Solvent | 0 | 0 | | 0 | | 0 | | 0 | |
| Total | 100.000004 | 100 | | 100 | | 100 | | 100 | |

## Table 4b (Xylenol optimisation results)

| | | Mode 5 | | Mode 6 | | Mode 7 | | Mode 8 | | Mode 9 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Peaks | Feed 2<br>SIG20042.D | 125°C Xylenol feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20060.D<br>Feed 2<br>79.93% Recovery | | 125°C Xylenol feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20070.D<br>Feed 2<br>71.96% Recovery | | 100°C Xylenol feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20078.D<br>Feed 2<br>75.3% Recovery | | 100°C Xylenol feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20096.D<br>Feed 2<br>87.91% Recovery | | 125°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>4 kg/hr reflux<br>40 kPa abs pressure<br>SIG20108.D<br>Feed 2<br>74.78% Recovery | |
| | Mass % | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining |
| 1 | 0.059153 | 0.069596 | 118% | 0.072962 | 123% | 0.073436 | 124% | 0.066732 | 113% | 0.069288 | 117% |
| 2a+b+c | 0.20022 | 0.23523 | 117% | 0.246177 | 123% | 0.247419 | 124% | 0.226631 | 113% | 0.242722 | 121% |
| 3 | 0 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 4 | 97.94589 | 98.87631 | 101% | 98.95481 | 101% | 98.93649 | 101% | 98.79258 | 101% | 98.80088 | 101% |
| 5 | 0.333754 | 0.288069 | 86% | 0.276133 | 83% | 0.273003 | 82% | 0.29195 | 87% | 0.290273 | 87% |
| 6 | 0.058015 | 0.048505 | 84% | 0.044641 | 77% | 0.043649 | 75% | 0.04666 | 80% | 0.046924 | 81% |
| 7 | 0.01305 | 0.006666 | 51% | 0.005337 | 41% | 0.004626 | 35% | 0.00651 | 50% | 0.006943 | 53% |
| 8 | 0.053524 | 0.050347 | 94% | 0.050105 | 94% | 0.050558 | 94% | 0.054283 | 101% | 0.051463 | 96% |
| 9 | 0.061945 | 0.036547 | 59% | 0.032915 | 53% | 0.034137 | 55% | 0.042382 | 68% | 0.04002 | 65% |
| 10 | 0.026563 | 0.006526 | 25% | 0.004153 | 16% | 0.005953 | 22% | 0.009384 | 35% | 0.008565 | 32% |
| 11 | 0.255379 | 0.073456 | 29% | 0.05553 | 22% | 0.05945 | 23% | 0.092734 | 36% | 0.091181 | 36% |
| 12 | 0.52088 | 0.265219 | 51% | 0.224428 | 43% | 0.236699 | 45% | 0.311294 | 60% | 0.292382 | 56% |
| 13 | 0.043873 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 15 | 0.105779 | 0.015499 | 15% | 0.009864 | 9% | 0.010371 | 10% | 0.019036 | 18% | 0.020221 | 19% |
| 14 | 0.174849 | 0.015761 | 9% | 0.010911 | 6% | 0.012163 | 7% | 0.023562 | 13% | 0.02396 | 14% |
| 16 | 0.00592 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 17 | 0.017051 | 0 | 0% | 0 | 0% | 0 | 0% | 0.003697 | 22% | 0.003287 | 19% |
| 18 | 0.058864 | 0 | 0% | 0 | 0% | 0 | 0% | 0.003178 | 5% | 0.003567 | 6% |
| 19 | 0.013843 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| Light Other | 0 | 0 | 0% | 0.002334 | | 0.002469 | | 0 | 0% | 0 | 0% |
| Heavy Other | 0.051718 | 0.01225 | 24% | 0.009685 | 19% | 0.009557 | 18% | 0.009367 | 18% | 0.008303 | 16% |
| Sol-vent | 0 | 0 | | 0 | | 0 | | 0 | | 0 | |
| Total | 100.0002 | 100 | | 100 | | 100 | | 100 | | 100 | |

## Table 4c (NMP/xylenol optimisation results)

| | | Mode 10 | | Mode 11 | | Mode 12 | |
|---|---|---|---|---|---|---|---|
| Peaks | Feed 2<br>SIG20042.D | 79°C NMP/Xylenol Feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20016.D<br>Feed 2<br>72.36% Recovery | | 85°C NMP/Xylenol Feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20026.D<br>Feed 2<br>74.69% Recovery | | 94°C NMP/Xylenol Feed T<br>25 kg/hr xylenol<br>1 kg/hr octene<br>4 kg/hr reflux<br>40 kPa abs pressure<br>SIG20025.D<br>Feed 2<br>74.43% Recovery | |
| | Mass % | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining |
| 1 | 0.059153 | 0.068183 | 115% | 0.06787 | 115% | 0.068946 | 117% |
| 2a+b+c | 0.20022 | 0.247758 | 124% | 0.236756 | 118% | 0.23278 | 116% |
| 3 | 0 | 0 | 0% | 0 | 0% | 0 | 0% |
| 4 | 97.94589 | 98.794988 | 101% | 98.816039 | 101% | 98.835538 | 101% |
| 5 | 0.333754 | 0.275408 | 83% | 0.282561 | 85% | 0.286731 | 86% |
| 6 | 0.058015 | 0.041837 | 72% | 0.042399 | 73% | 0.042902 | 74% |
| 7 | 0.01305 | 0.004746 | 36% | 0.004846 | 37% | 0.005136 | 39% |
| 8 | 0.053524 | 0.048581 | 91% | 0.048472 | 91% | 0.047736 | 89% |
| 9 | 0.061945 | 0.039993 | 65% | 0.041367 | 67% | 0.040092 | 65% |
| 10 | 0.026563 | 0.011415 | 43% | 0.011054 | 42% | 0.010241 | 39% |
| 11 | 0.255379 | 0.094981 | 37% | 0.090821 | 36% | 0.086974 | 34% |
| 12 | 0.52088 | 0.274353 | 53% | 0.273175 | 52% | 0.265979 | 51% |
| 13 | 0.043873 | 0.009736 | 22% | 0.007888 | 18% | 0.006977 | 16% |
| 15 | 0.105779 | 0.027546 | 26% | 0.023515 | 22% | 0.021484 | 20% |
| 14 | 0.174849 | 0.038253 | 22% | 0.030932 | 18% | 0.02758 | 16% |
| 16 | 0.00592 | 0 | 0% | 0 | 0% | 0 | 0% |
| 17 | 0.017051 | 0.004942 | 29% | 0.004493 | 26% | 0.004241 | 25% |
| 18 | 0.058864 | 0.00797 | 14% | 0.005254 | 9% | 0.004628 | 8% |
| 19 | 0.013843 | 0 | 0% | 0 | 0% | 0.002693636 | 19% |
| Light Other | 0 | 0.002838 | | 0.002459 | | 0.002209 | |
| Heavy Other | 0.051718 | 0.006472 | 13% | 0.0101 | 20% | 0.009827 | 19% |
| Solvent | 0 | 0 | | 0 | | 0 | |
| Total | 100.00027 | 100 | | 100 | | 100 | |

## Table 4d (Best solvent optimisation results)

| | | Mode 13 | | Mode 14 | | Mode 15 | | Mode 16 | |
|---|---|---|---|---|---|---|---|---|---|
| Peaks | Feed 2<br>SIG20042.D | 125°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>4 kg/hr reflux<br>40 kPa abs pressure<br>SIG20060.D<br>Feed 2<br>88.01% Recovery | | 125°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>2 kg/hr reflux<br>40 kPa abs pressure<br>SIG20061.D<br>Feed 2<br>86.3% Recovery | | 125°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>6 kg/hr reflux<br>40 kPa abs pressure<br>SIG20070.D<br>Feed 2<br>86.45% Recovery | | 132°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>6 kg/hr reflux<br>40 kPa abs pressure<br>SIG20111.D<br>Feed 2<br>88.95% Recovery | |
| | Mass % | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining |
| 1 | 0.059153 | 0.06905 | 117% | 0.067366 | 114% | 0.065877 | 111% | 0.065855 | 111% |
| 2a+b+c | 0.20022 | 0.232541 | 116% | 0.222651 | 111% | 0.222536 | 111% | 0.221919 | 111% |
| 3 | 0 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 4 | 97.94589 | 98.65135 | 101% | 98.61409 | 101% | 98.63369 | 101% | 98.65713 | 101% |
| 5 | 0.333754 | 0.299668 | 90% | 0.309054 | 93% | 0.304142 | 91% | 0.305237 | 91% |
| 6 | 0.058015 | 0.050745 | 87% | 0.052969 | 91% | 0.052147 | 90% | 0.051781 | 89% |
| 7 | 0.01305 | 0.008033 | 62% | 0.009432 | 72% | 0.008882 | 68% | 0.008685 | 67% |
| 8 | 0.053524 | 0.050592 | 95% | 0.0493 | 92% | 0.051597 | 96% | 0.050907 | 95% |
| 9 | 0.061945 | 0.043657 | 70% | 0.045513 | 73% | 0.047075 | 76% | 0.045844 | 74% |
| 10 | 0.026563 | 0.012111 | 46% | 0.012028 | 45% | 0.012732 | 48% | 0.012288 | 46% |
| 11 | 0.255379 | 0.124385 | 49% | 0.134262 | 53% | 0.128618 | 50% | 0.124764 | 49% |
| 12 | 0.52088 | 0.337992 | 65% | 0.347318 | 67% | 0.352978 | 68% | 0.348912 | 67% |
| 13 | 0.043873 | 0.008856 | 20% | 0.008595 | 20% | 0.007518 | 17% | 0.006639 | 15% |
| 15 | 0.105779 | 0.034285 | 32% | 0.039085 | 37% | 0.033646 | 32% | 0.031996 | 30% |
| 14 | 0.174849 | 0.045206 | 26% | 0.048366 | 28% | 0.042176 | 24% | 0.039456 | 23% |
| 16 | 0.00592 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 17 | 0.017051 | 0.004991 | 29% | 0.005633 | 33% | 0.005222 | 31% | 0.004674 | 27% |
| 18 | 0.058864 | 0.008519 | 14% | 0.010949 | 19% | 0.007969 | 14% | 0.006803 | 12% |
| 19 | 0.013843 | 0.003848 | 28% | 0.004566 | 33% | 0.003658 | 26% | 0.003356 | 24% |
| Light Other | 0 | 0.006382 | | 0.006046 | | 0.00912 | | 0.007419 | |
| Heavy Other | 0.051718 | 0.001189 | 2% | 0.001808 | 3% | 0.003327 | 6% | 0 | 0% |
| Solvent | 0 | 0 | | 0 | | 0 | | 0 | |
| Total | 100.0003 | 100 | | 100 | | 100 | | 100 | |

## Table 4d (Best solvent optimisation results) continued

| | | Mode 17 Sample 1 | | Mode 17 Sample 2 | | Mode 17 Sample 3 | | Mode 17 Sample 4 | |
|---|---|---|---|---|---|---|---|---|---|
| Peaks | Feed 2<br>SIG20042.D | 140°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>6 kg/hr reflux<br>40 kPa abs pressure<br>SIG20127.D<br>Feed 2<br>84.12% Recovery | | 140°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>6 kg/hr reflux<br>40 kPa abs pressure<br>SIG20128.D<br>Feed 2<br>85.21% Recovery | | 140°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>6 kg/hr reflux<br>40 kPa abs pressure<br>SIG20126.D<br>Feed 2<br>84.12% Recovery | | 140°C Xylenol feed T<br>30 kg/hr xylenol<br>2 kg/hr octene<br>6 kg/hr reflux<br>40 kPa abs pressure<br>SIG20125.D<br>Feed 2<br>83.80% Recovery | |
| | Mass % | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining | Mass % | % Remaining |
| 1 | 0.059153 | 0.067768 | 115% | 0.0674 | 114% | 0.072643 | 123% | 0.072409 | 122% |
| 2a+b+c | 0.20022 | 0.229284 | 115% | 0.231284 | 116% | 0.231513 | 116% | 0.238754 | 119% |
| 3 | 0 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 4 | 97.94589 | 98.72006 | 101% | 98.74585 | 101% | 98.70918 | 101% | 98.6718 | 101% |
| 5 | 0.333754 | 0.298828 | 90% | 0.299062 | 90% | 0.30145 | 90% | 0.302659 | 91% |
| 6 | 0.058015 | 0.05034 | 87% | 0.049929 | 86% | 0.052828 | 91% | 0.053513 | 92% |
| 7 | 0.01305 | 0.007674 | 59% | 0.008106 | 62% | 0.009116 | 70% | 0.009005 | 69% |
| 8 | 0.053524 | 0.050144 | 94% | 0.049592 | 93% | 0.051394 | 96% | 0.052385 | 98% |
| 9 | 0.061945 | 0.041698 | 67% | 0.04145 | 67% | 0.045685 | 74% | 0.046764 | 75% |
| 10 | 0.026563 | 0.010221 | 38% | 0.009126 | 34% | 0.00932 | 35% | 0.014228 | 54% |
| 11 | 0.255379 | 0.109725 | 43% | 0.105879 | 41% | 0.108428 | 42% | 0.107707 | 42% |
| 12 | 0.52088 | 0.318086 | 61% | 0.30497 | 59% | 0.312339 | 60% | 0.318161 | 61% |
| 13 | 0.043873 | 0.006108 | 14% | 0 | 0% | 0.006146 | 14% | 0.006701 | 15% |
| 15 | 0.105779 | 0.027205 | 26% | 0.02666 | 25% | 0.032671 | 31% | 0.030117 | 28% |
| 14 | 0.174849 | 0.032857 | 19% | 0.032308 | 18% | 0.027586 | 16% | 0.034691 | 20% |
| 16 | 0.00592 | 0 | 0% | 0 | 0% | 0 | 0% | 0 | 0% |
| 17 | 0.017051 | 0.003797 | 22% | 0.004365 | 26% | 0.004953 | 29% | 0.007026 | 41% |
| 18 | 0.058864 | 0.005557 | 9% | 0.00567 | 10% | 0.006006 | 10% | 0.007547 | 13% |
| 19 | 0.013843 | 0.002658 | 19% | 0.002591 | 19% | 0.003448 | 25% | 0.003404 | 25% |
| Light Other | 0 | 0.006455 | | 0.006105 | | 0.0066 | | 0.011322 | |
| Heavy Other | 0.051718 | 0.005419 | 10% | 0.003486 | 7% | 0.0024 | 5% | 0.007004 | 14% |
| Solvent | 0 | 0 | | 0 | | 0 | | 0 | |
| Total | 100.0003 | 100 | | 100 | | 100 | | 100 | |

Figure 4a : Extraction of component 2a+b+c during pilot plant test work

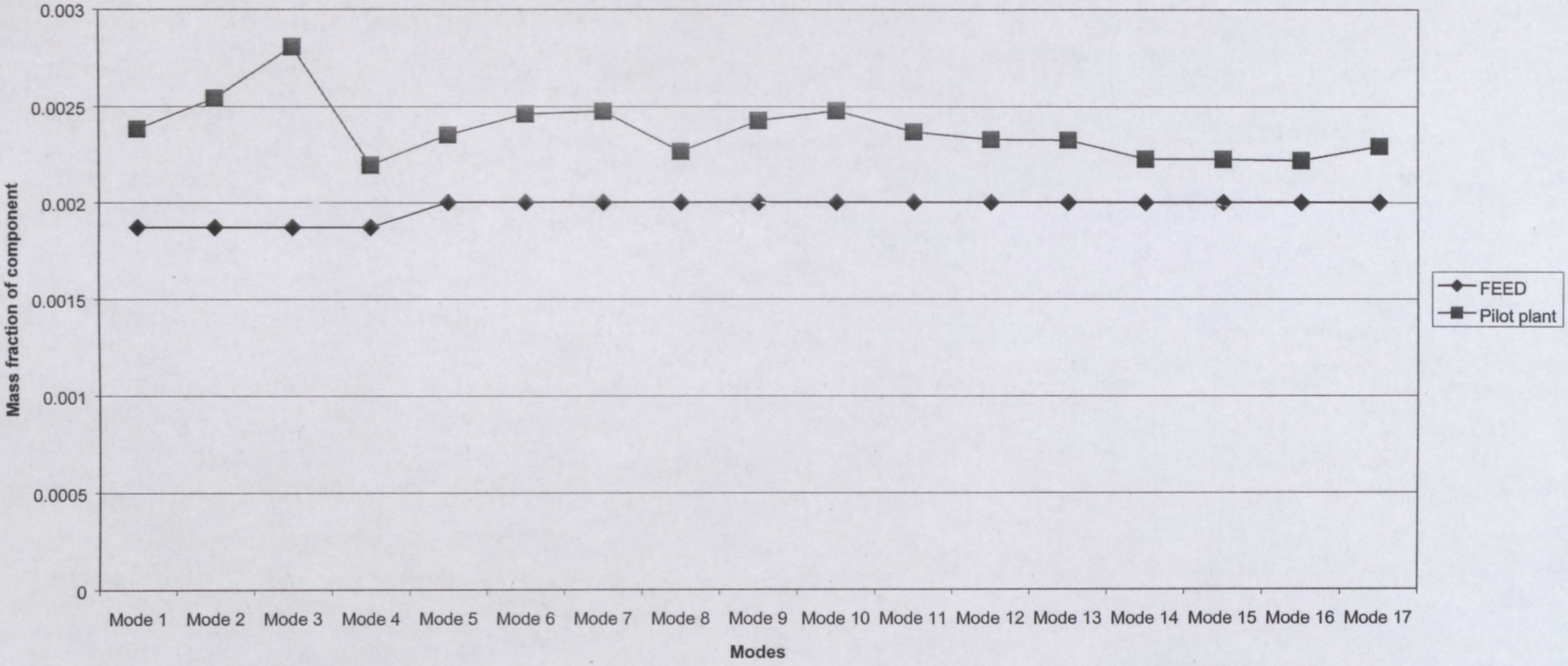


Figure 4b : Concentration of 1-octene during pilot plant test work

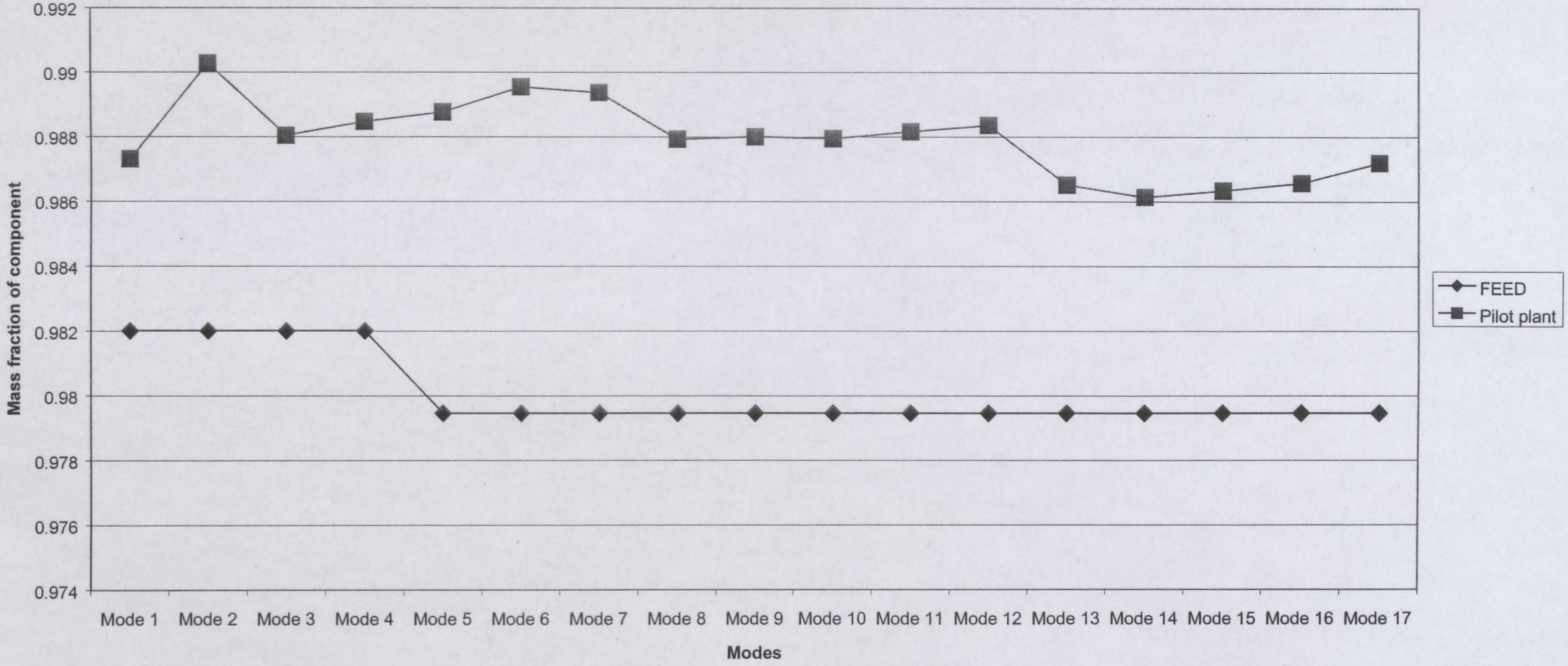


Figure 4c : Extraction of component 5 during pilot plant test work

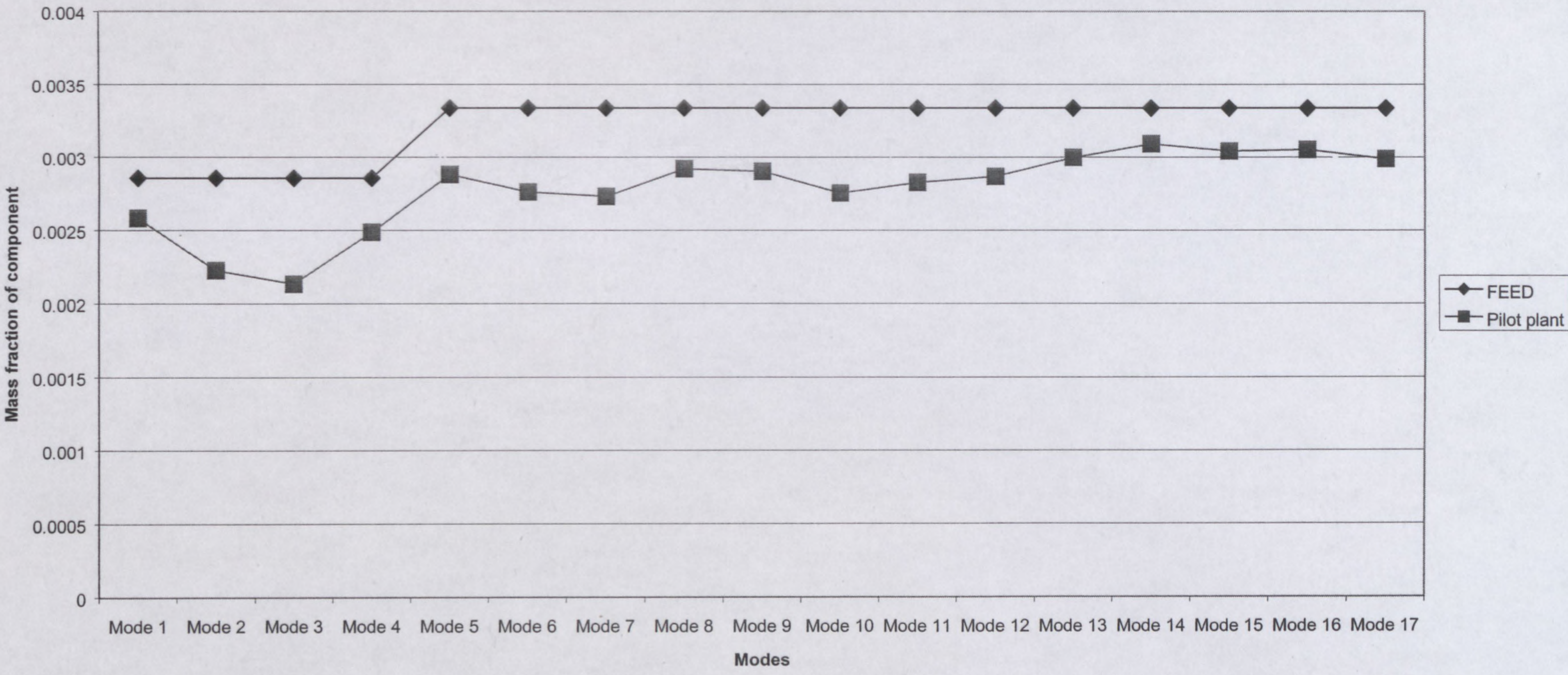


Figure 4d : Extraction of component 11 during pilot plant test work

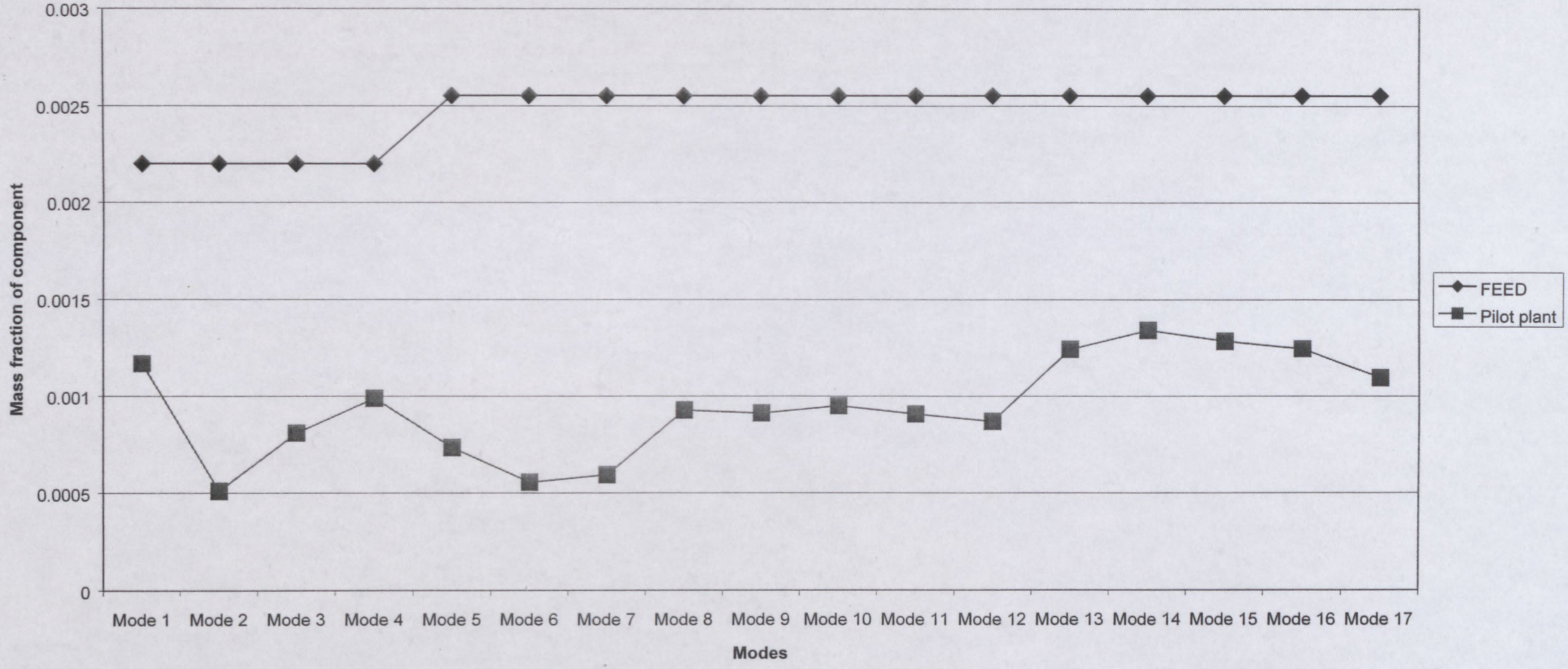


Figure 4e : Extraction of component 12 during pilot plant test work

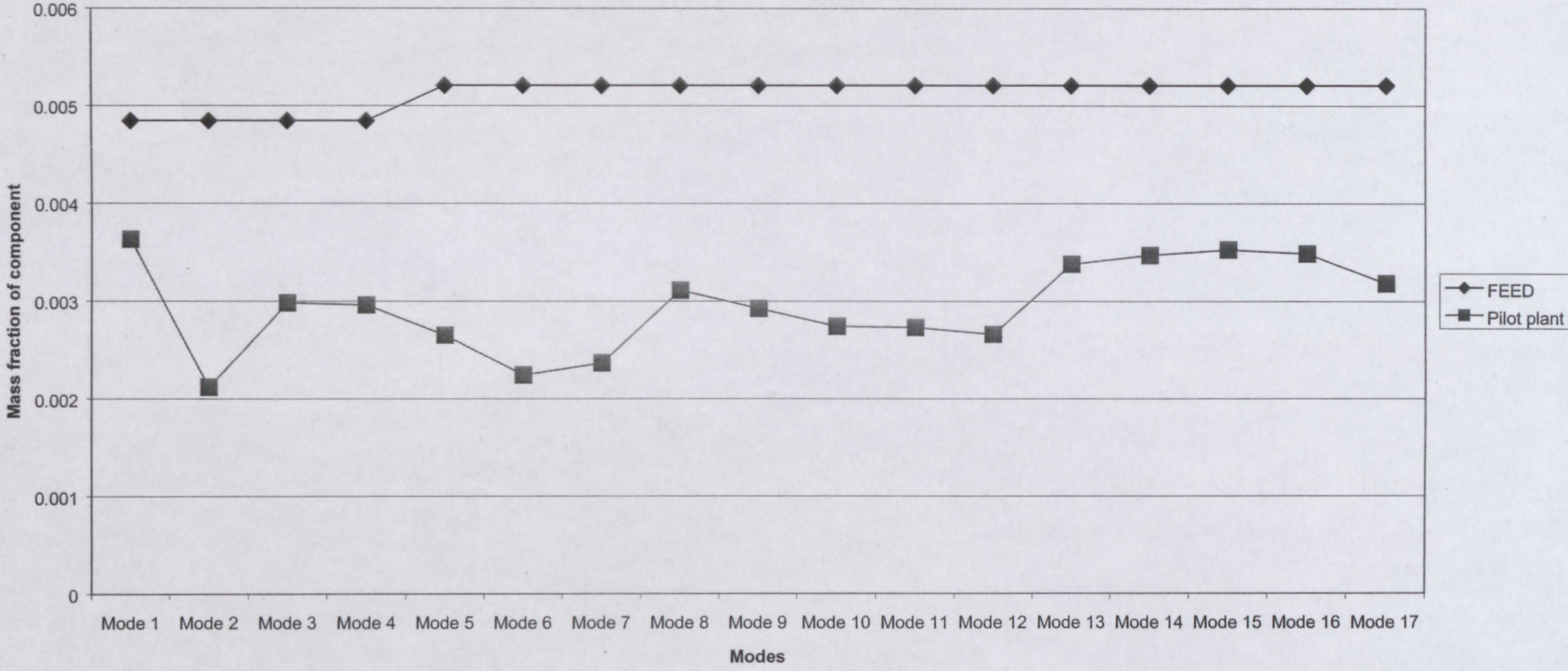


Figure 4f : Extraction of component 14+15 during pilot plant test work

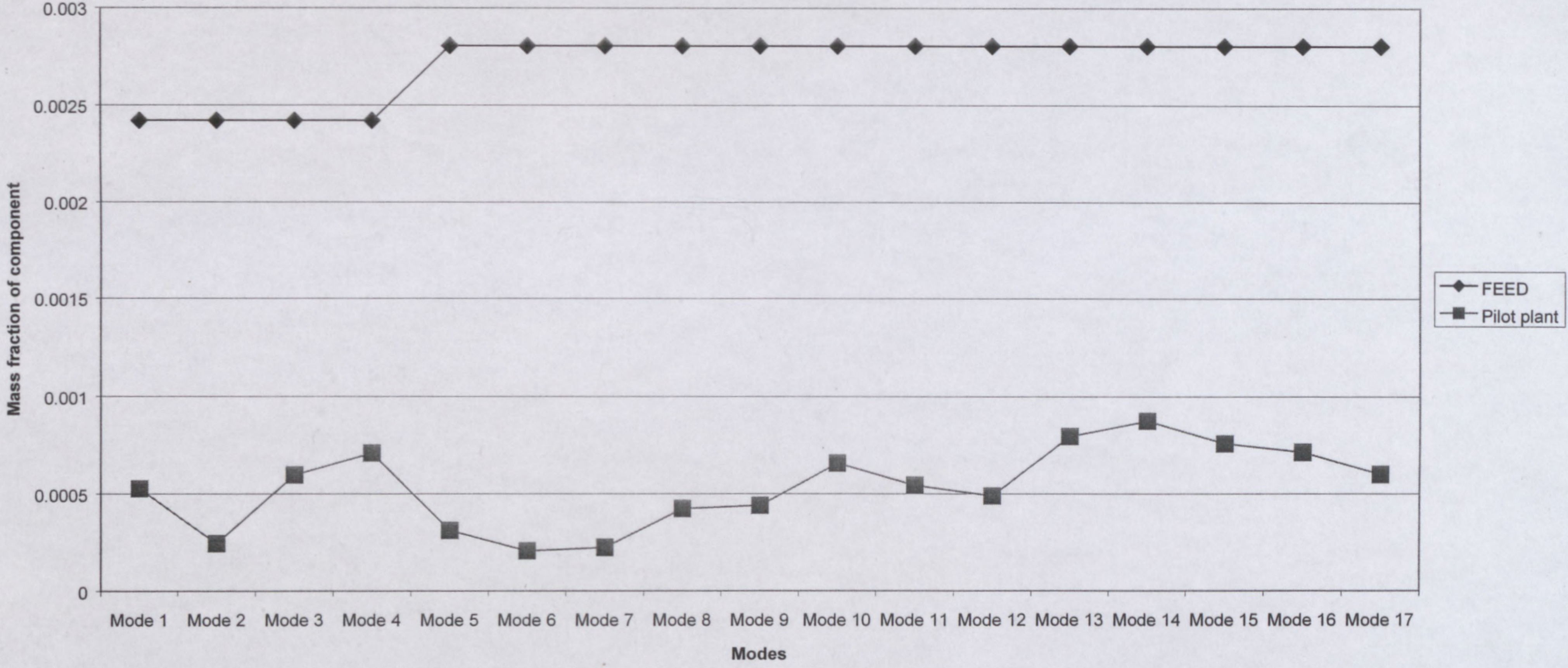


Figure 4g : Extraction of component 18 during pilot plant test work

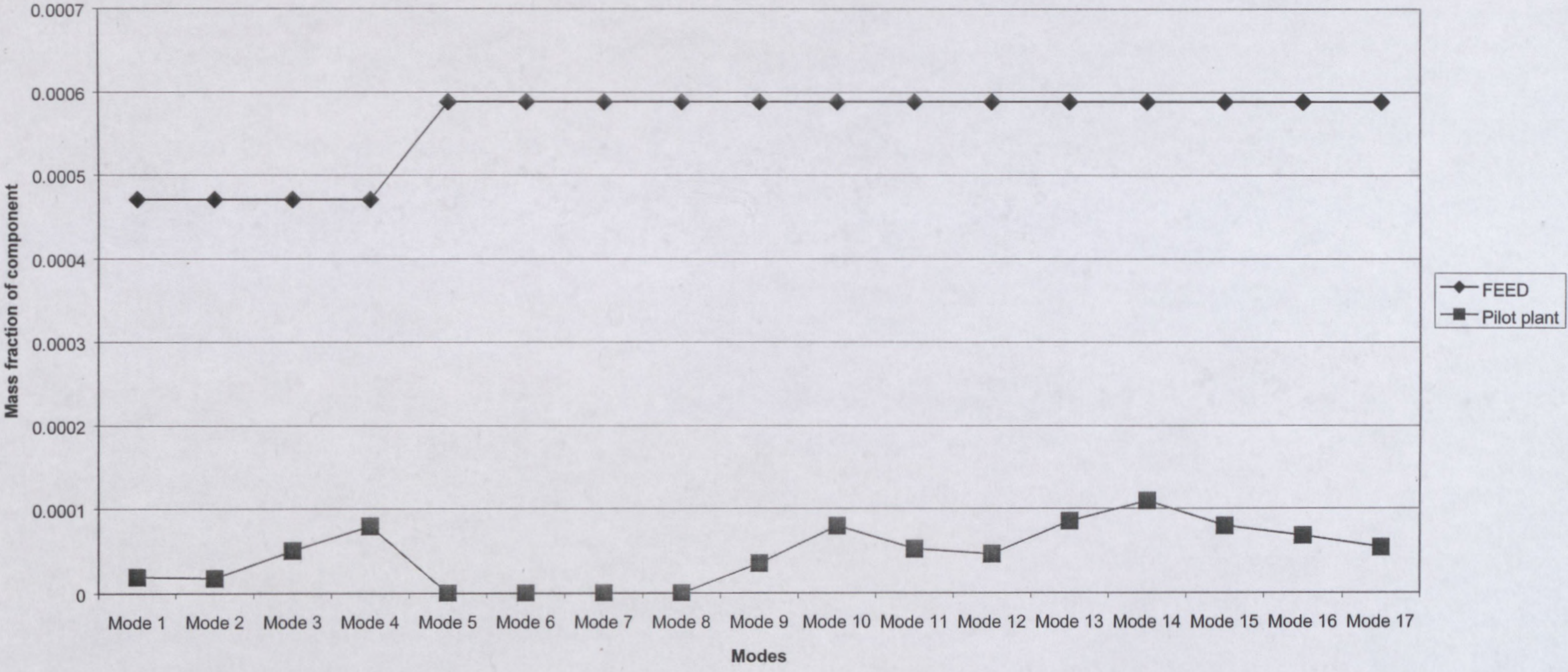
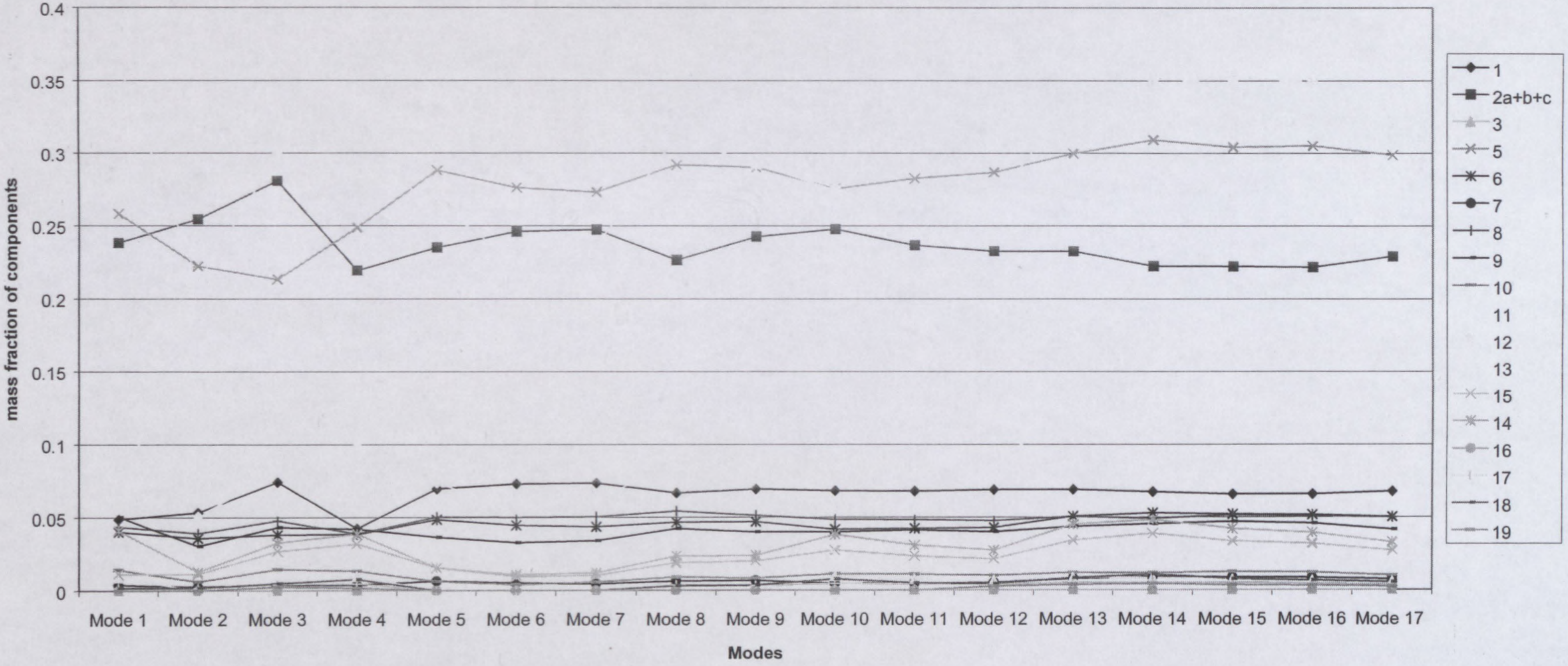


Figure 4h : Extraction of all the components during pilot plant test work



## 4.1 Solvent recovery

The NMP that was used for this project was 99.9% pure. The xylenol that was used for this project was a mixture of light xylenol high boiling tar acids. The composition of the solvent is indicated below:

| **Component** | **Area %** |
|---|---|
| Naphthalene | 0.91 |
| Benzothiophene | 0.0731 |
| Methyl-Naphthalene | 0.0741 |
| 2,6 xylenol | 0.448 |
| Ethyl-Phenol | 32.046 |
| 2,5 xylenol | 15.814 |
| 2,4 xylenol | 36.416 |
| o-cresol | 7.54 |
| 3,5 xylenol | 6.68 |
| **Total** | **100.0012** |

Only the xylenol that was used in the extractive distillation process was recovered in a separate distillation column - the alpha olefins pilot plant distillation "A" column.

NMP was only used for mode 1. The 1-octene-contaminated-NMP that was accumulated during this project was added to the rest of the contaminated NMP that was accumulated during previous piloting.

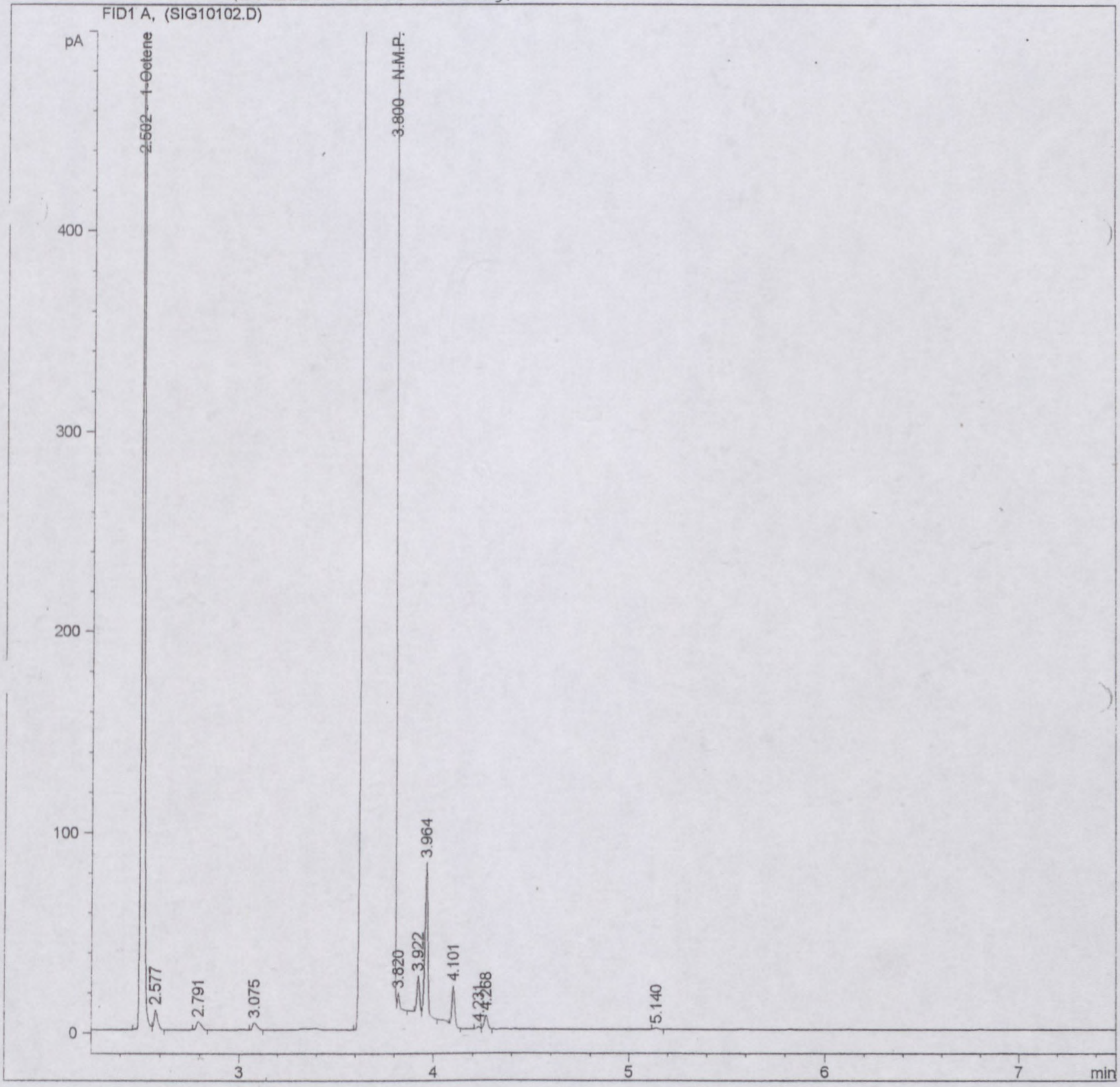
The solvent mixture (NMP/xylenol) that was used in modes 4 and 10 –12 was not recovered due to:

- The difficulty of the separation
- The small amount of the solvent that was available
- The results indicated that the mixture performed worse than xylenol

GC-traces of the 1-octene-contaminated NMP, xylenol and NMP/xylenol are attached in Appendix 4a, 4b and 4c respectively.

## APPENDIX 4a : 1-octene-contaminated NMP

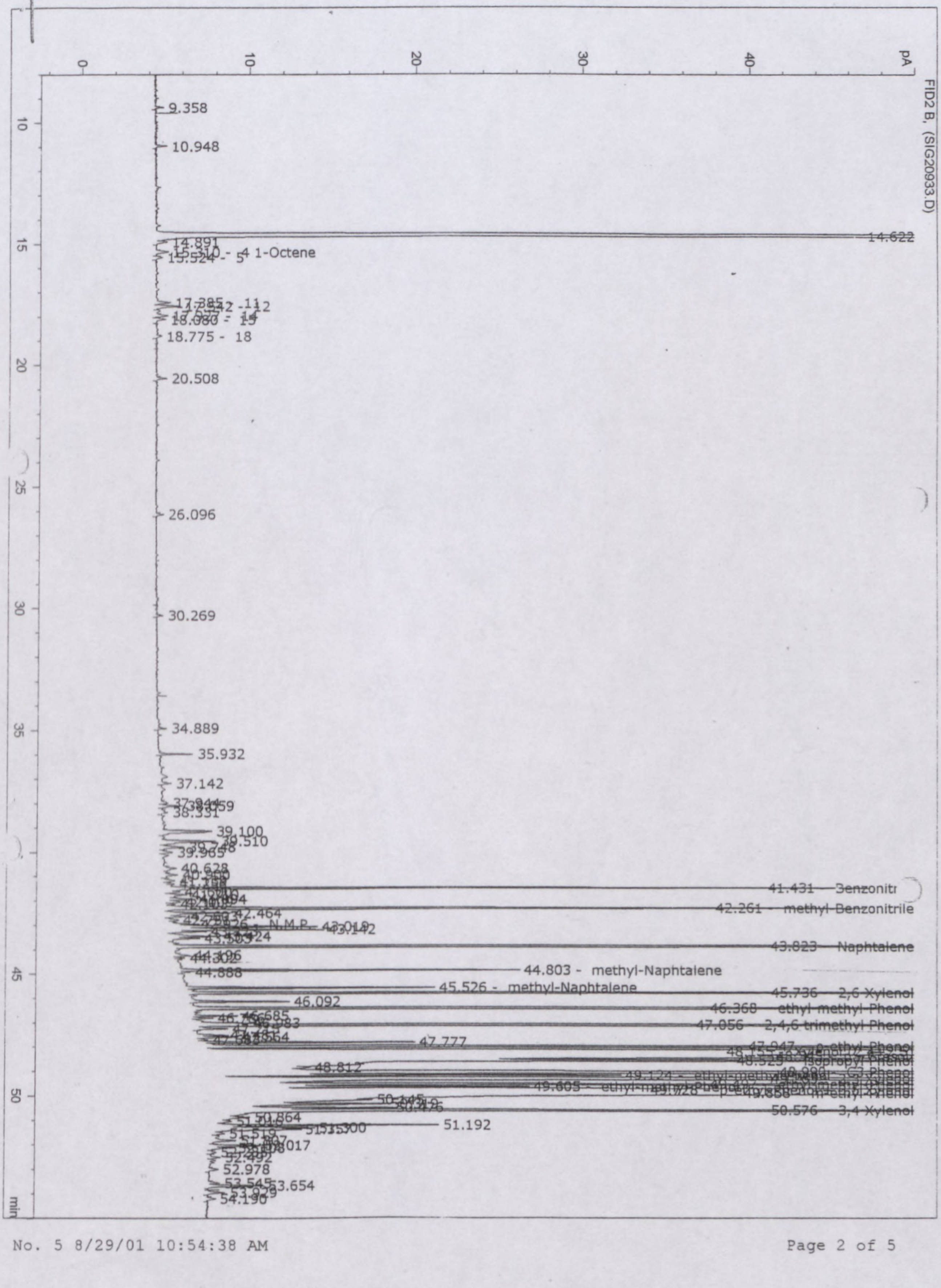
```
Data File C:\HPCHEM\3\DATA\SIG10102.D

   MCD 110 NMP Btms
   16/09/01
   01:00

   1-OCTENE=__________%

   NMP     =__________%

   =====================================================================
   Injection Date    : 9/16/01 1:19:04 AM
   Sample Name       :                              Location : Vial 1
   Acq. Operator     :                                   Inj :   1
                                                  Inj Volume : Manually
   Method            : C:\HPCHEM\3\METHODS\110-BOTT.M
   Last changed      : 9/15/01 7:05:48 AM
                       (modified after loading)
```



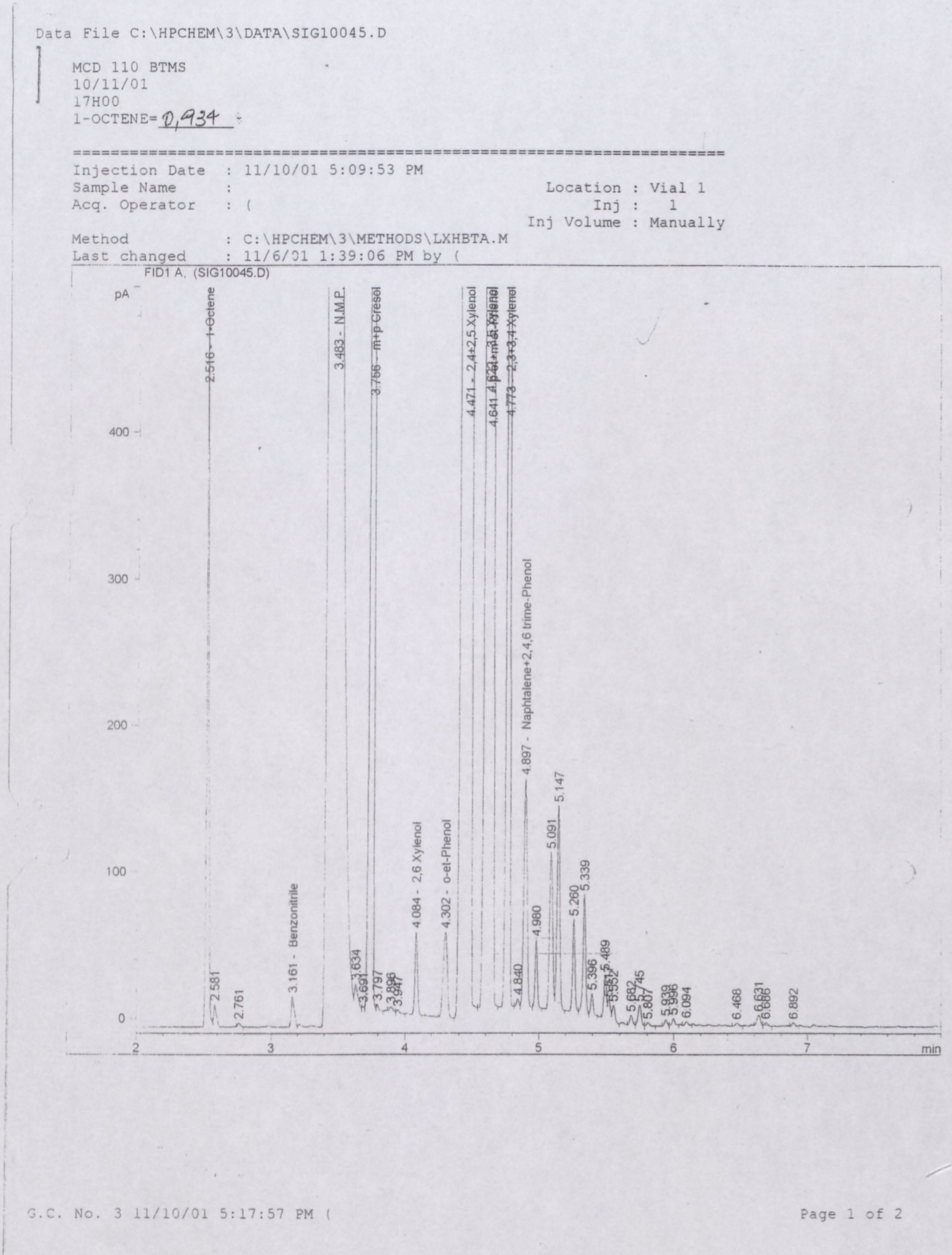
G.C. No. 3 9/16/01 1:26:38 AM                                  Page 1 of 2

## APPENDIX 4b : 1-octene-contaminated xylenol

Data File C:\HPCHEM\1\DATA\SIG20933.D



## APPENDIX 4c : 1-octene-contaminated NMP/xylenol



```
Data File C:\HPCHEM\3\DATA\SIG10045.D

   MCD 110 BTMS
   10/11/01
   17H00
   1-OCTENE= 0,934

   =====================================================================
   Injection Date  : 11/10/01 5:09:53 PM
   Sample Name     :                                  Location : Vial 1
   Acq. Operator   : (                                     Inj :   1
                                                    Inj Volume : Manually
   Method          : C:\HPCHEM\3\METHODS\LXHBTA.M
   Last changed    : 11/6/01 1:39:06 PM by (
```

```
G.C. No. 3 11/10/01 5:17:57 PM (                          Page 1 of 2
```

### 4.1.1 Column configuration

The alpha olefins A-column is relative large as compared to the extractive distillation column, i.e. it has an internal diameter of 320 mm and has a liquid hold-up of approximately 150 litres. This column was used as it was the only column available and suitable at the time.

No design data was collected during the solvent recovery piloting. However, from previous piloting it is known that heavy components build up when the system is run in a closed loop. Thus, a purge stream is required in the process.

The recovery of the solvent had to be done in batch modes. The bottoms product from the extractive distillation step was collected in an iso-container and when the amount of product was sufficient, the recovery-column was commissioned.

The column configuration was relatively simple in distillation terms. The following configuration was required:

- Feed rate of 100 kg/hr, from an iso-container via a centrifugal pump.
- No external reflux was required, because only about 1% of the feed went overheads.
- Vacuum of 20kpa abs.

The P&ID of the alpha olefins A-column pilot plant is attached as Fig. 4.1.

The feed to the column was the bottoms from the extractive distillation step. The bottoms contained 0.8 - 1% 1-octene.

The reboiler was filled with the 1-octene-contaminated-solvent to a 60% level before heating commenced. No reflux was obtained since only 1% of the feed reported to the overheads. The bottoms product from the recovery column was circulated over the feed container until specification was achieved.

The conditions during stable and on-specification operation are indicated below:

| **Parameter** | **Xylenol recovery Conditions** | **NMP recovery Conditions** |
|---|---|---|
| Pressure | 20 kPa abs | 20 kPa abs |
| Feed rate | 100 kg/h | 100 kg/h |
| Reboiler temperature | 166.37°C | 158°C |
| Top temperature | 139.86°C | 138°C |
| Reflux rate | 0 kg/h | 0 kg/h |
| Distillate | 0 kg/h | 0 kg/h |
| Bottoms rate | 99 kg/h | 99 kg/h |

The specification of light components in the bottoms was less than 0.1%, which translates to a recovery of 99.9%. The bottoms product was analysed and it contained 0.002% of light components.

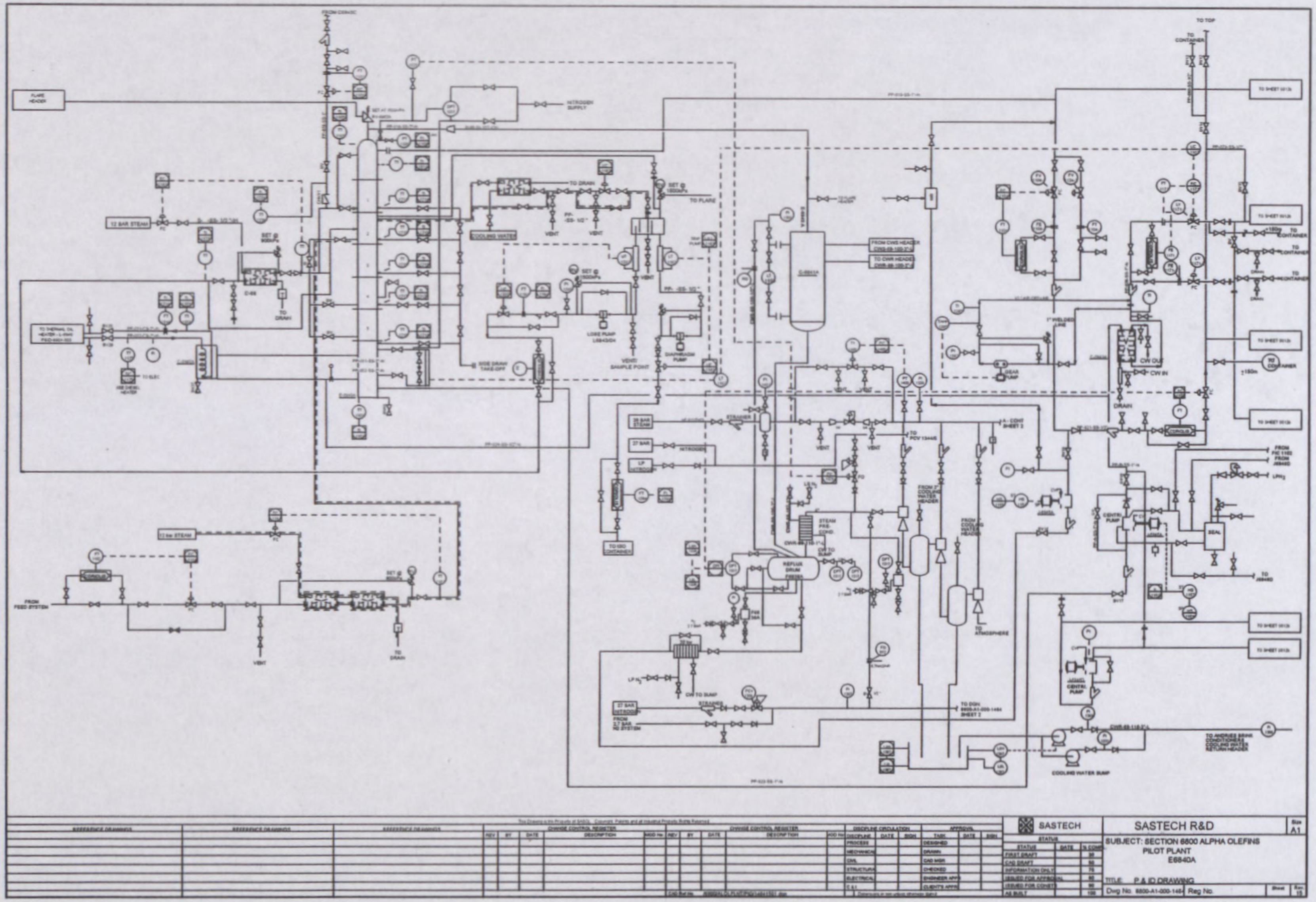


Fig. 4.1 P&ID of the alpha olefins A-column pilot plant.

## 4.2 Discussion

### Evaluation of the base run results

Table 4a compares the base runs that were performed at the NMP optimised conditions. Mode 3, however, was performed at a 4 : 1 (reflux : feed) ratio, as opposed to a 2 : 1 ratio. The reason for this increase was to evaluate whether there would be a significant improvement in extraction power as a result of increased external reflux.

Reflux in this extractive distillation column is necessary to ensure that the relative volatility between the octene and the poisons is enhanced. The reflux can be supplied by either external reflux or cool solvent feed (causing internal reflux). External reflux is required to ensure successful removal of the solvent from the top section of the column. The advantage of a higher reflux must be balanced against the disadvantage of a lower solvent concentration in the column and the reduction of relative volatility [6].

Comparing Mode 3 to Mode 2, it is clear that the increased reflux : feed ratio, leading to a lower solvent concentration in the column, did not improve the separation.

The solvent feed temperature for Mode 1 was 80°C. The solvent feed temperature for Mode 2 and 3 was 113°C and 96.5°C during Mode 4. The increased solvent feed temperatures of Modes 2, 3 and 4 correlates to the solvent feed temperature of Mode 1 in terms of the difference in specific heat from the bubble point of the solvent down to respective feed temperature.

Comparing Mode 2 to Mode 1, it is noticed that NMP is more effective in the light end (peaks 1 & 2a+b+c) and the heavier end (peaks 17 – end), while xylenol is significantly more effective in the middle (peaks 5 – 14).

Comparing Mode 2 to Mode 4, it is observed that the NMP/xylenol mixture performed very well in the light end (peaks 1 & 2a+b+c). The mixture performed better than NMP but worse than xylenol (peaks 5 – 15). The solvent mixture performed worse than both clean NMP and xylenol in terms of the heavy end (peaks 17 – end).

From the above results, it is concluded that xylenol performed better than NMP as well as the NMP/xylenol mixture.

**Evaluation of the xylenol optimisation results**

As mentioned before, the xylenol and the NMP/xylenol conditions had to be optimised. Table 4b illustrates the xylenol optimised results. The parameters that were adjusted were:

- the solvent feed temperature
- the 1-octene recovery
- the solvent : feed ratio

Comparing Mode 5 to Mode 6, the 1-octene recovery was the only parameter that was changed. A lower recovery enhanced the separation in the middle and heavy end, but not in the light end (peaks 1 & 2). The same comparison was done during Mode 7 & 8, but the solvent feed temperature was decreased from 125°C to 100°C. In terms of recovery, the same outcome was observed, i.e. a lower recovery resulted in better separation. In terms of commercialisation, it will not be suitable to operate a column at a low recovery. For this reason, the results of Mode 6 and 7 may be considered as irrelevant.

Comparing the results in terms of solvent feed temperature, it is clear that the higher solvent temperature enhanced the separation. By increasing the solvent temperature, the degree of sub-cooling of the solvent decreased, and reduced the internal reflux in the column. The result is that there are lower 1-octene concentrations in the extractive distillation section of the column, leading to a higher solvent : feed ratio. This leads to better separation.

During Mode 9 the solvent : feed ratio was decreased from 25 : 1 to 15 : 1. The reflux : feed ratio remained constant. Comparing the results of Mode 9 to the results of Mode 5 and Mode 8, it is apparent that the extraction was better than Mode 8, but worse than Mode 5.

### Evaluation of the NMP/xylenol mixture optimisation results

Table 4c illustrates the NMP/xylenol optimised results. The following parameters were adjusted:

- the solvent feed temperature
- the reflux : feed ratio

Comparing Mode 11 to Mode 10, it is clear that the increased solvent temperature increased the separation slightly, especially in the heavier end (peak 13 – end). During Mode 12, the solvent feed temperature was increased further, and the reflux : feed ratio was also increased from 2 : 1 to 4 : 1. This resulted in better separation than both Modes 10 and 11.

### Comparison of the optimised results of xylenol to the NMP/xylenol mixture

Xylenol performed better as an extraction solvent than the NMP/xylenol mixture. In particular, mode 7 (xylenol) vs. mode 11 (NMP/xylenol), since these modes were conducted at similar conditions i.t.o. flows, 1-octene recovery and reflux-ratio. The NMP/xylenol mixture performed worse than the xylenol, but better than NMP (mode 11 vs. mode 1).

### Evaluation of the best solvent optimisation results

It was decided to optimise the xylenol conditions further and to evaluate the effect of altering the following parameters:

- reflux : feed ratio
- solvent feed temperature

Further optimisation tests were conducted with xylenol at a 1-octene recovery of between 85 and 90%. The results of the further optimised conditions are given in Table 4d.

During Modes 13, 14 and 15, the effect of the reflux : feed ratio was evaluated. Comparing the results of Mode 13 to Mode 14, a 2 : 1 reflux : feed ratio resulted in better separation than the 1 : 1 reflux : feed ratio. When the reflux : feed ratio is increased further to 3 : 1 (Mode 15), the separation is better in the heavier end (from peak 13) as well as the lighter end (peaks 1 and 2a+b+c). Comparing Mode 15 to Mode 13 and 14 i.t.o. the middle part of the spectrum, the separation of Mode 15 was better than Mode 14, but worse than Mode 13. Thus, the higher reflux : feed ratio proved to increase separation.

During Mode 16 and 17, the effect of increasing the solvent feed temperature even further was evaluated. The solvent feed temperature was increased from 125°C to 132°C in Mode 16, and increased further from 132°C to 140°C in Mode 17. The separation increased with the increase of solvent feed temperature in both cases. It was decided to prepare a 100-litre sample at the Mode 17-conditions.

## 4.3 Chapter conclusion

Evaluating the 1-octene concentration profile in figure 4b, it is concluded that xylenol performed better as an extraction solvent than NMP as well as the NMP/xylenol mixture. The NMP/xylenol mixture performed worse than the xylenol, but better than NMP.

From figure 4h, which compares the concentration-profiles of all the components to the different modes, it is clear that xylenol has a big impact on the concentration-profile of the components, especially modes 2, 5, and 6.

The extraction power is increased significantly by increasing the solvent feed temperature, resulting in a lower internal 1-octene concentration and a higher solvent : feed ratio.

# CHAPTER 5

# SIMULATION

An Aspen Plus (version 10.2) simulation model was generated for the extractive distillation process and the predictions of the model were compared to the data obtained from the pilot plant test work.

The accuracy of the model was verified over a wide range of conditions. Seventeen simulations were generated to predict the pilot plant test work.

## 5.1 Modelling phase equilibrium

The calculation of accurate thermodynamic property data in a simulation is extremely important. The most important thermodynamic property that is calculated by a distillation simulation is phase equilibrium. Phase equilibrium data describes the separability of the mixture. It is also important to accurately calculate enthalpy data for the vapour and liquid mixtures since these determine phase-flow rates [2]. Other physical properties such as densities, viscosities and surface tensions are also important in distillation calculations, and needs to be predicted accurately.

The most basic relationship of vapour and liquid phases in equilibrium is [7],

$$f^v{}_i = f^l{}_i$$

where $f^v{}_i$ = fugacity of component i in the vapour phase
$f^l{}_i$ = fugacity of component i in the liquid phase

There are two basic types of methods that are used to calculate the fugacities from the phase equilibrium, i.e. the equations of state (EOS) method and the activity coefficient method [7].

When the activity coefficient method is used, the activity coefficient correlates the non-ideality of the liquid phase(s) and the fugacity coefficients correlate the non-ideality of the vapour [2]. This method is accurate for systems at low and moderate pressures, over narrow temperature ranges. The predictive equations of state that can handle polar systems should be used for highly non-ideal chemical systems at high pressures [2].

When the equations of state method is used, a single equation of state is used to represent the behaviour for both phases. This method can be applied to wide pressure and temperature ranges, including critical and sub-critical conditions [2].

To accurately simulate non-ideal systems, binary interaction parameters must be obtained from experimental vapour-liquid equilibrium data. The simpler equations of state cannot represent highly non-ideal chemical systems, as a result of the assumptions that were made when these equations were formulated [2]. When highly non-ideal chemical systems are simulated, the activity coefficient method should be used at low pressures and the predictive equations of state should be used at high pressures [2].

### 5.1.1 Choosing a property method

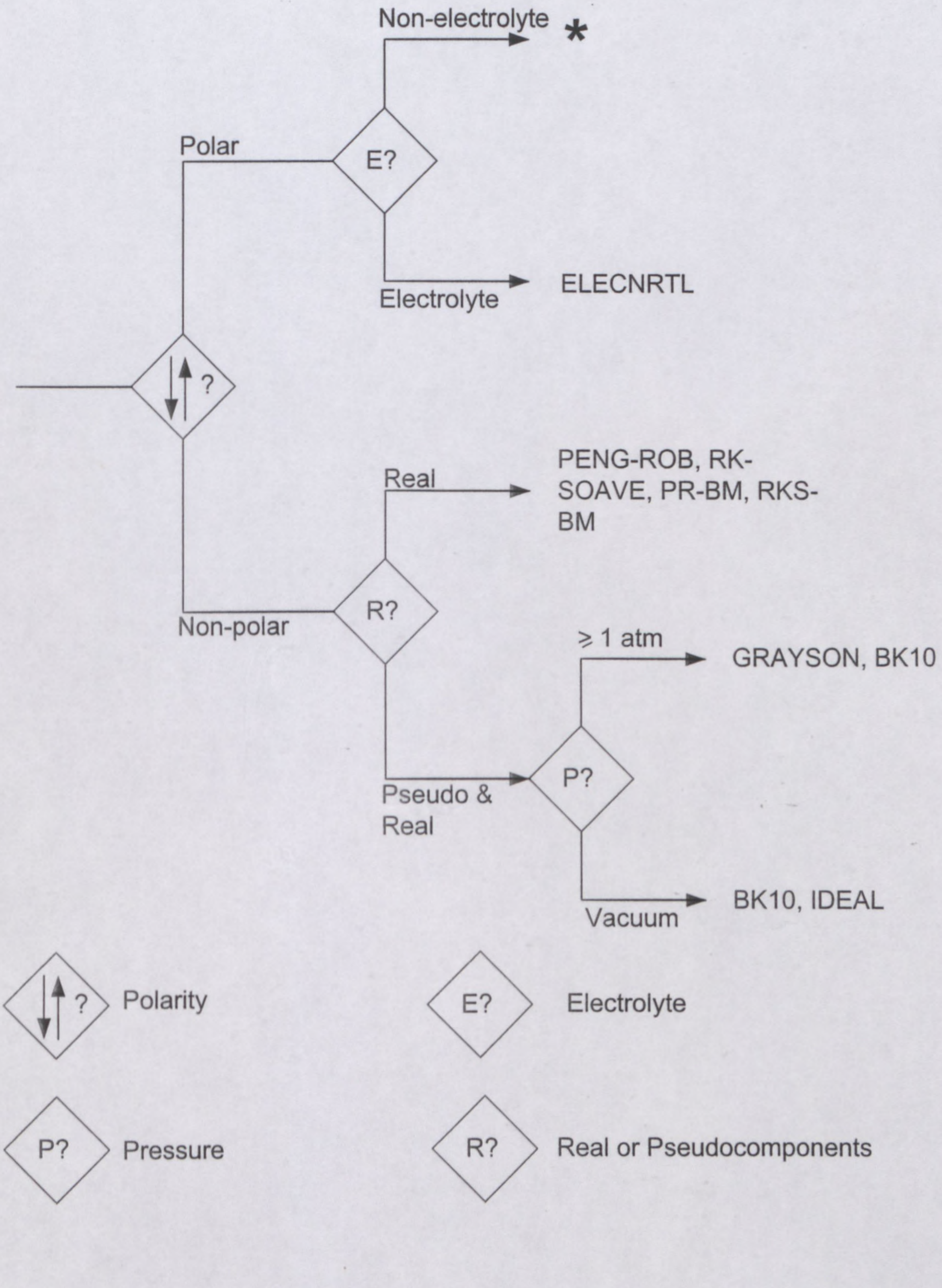
The property methods can be categorised into four groups [7]:

- Ideal
- Equation of state
- Activity coefficient
- Special

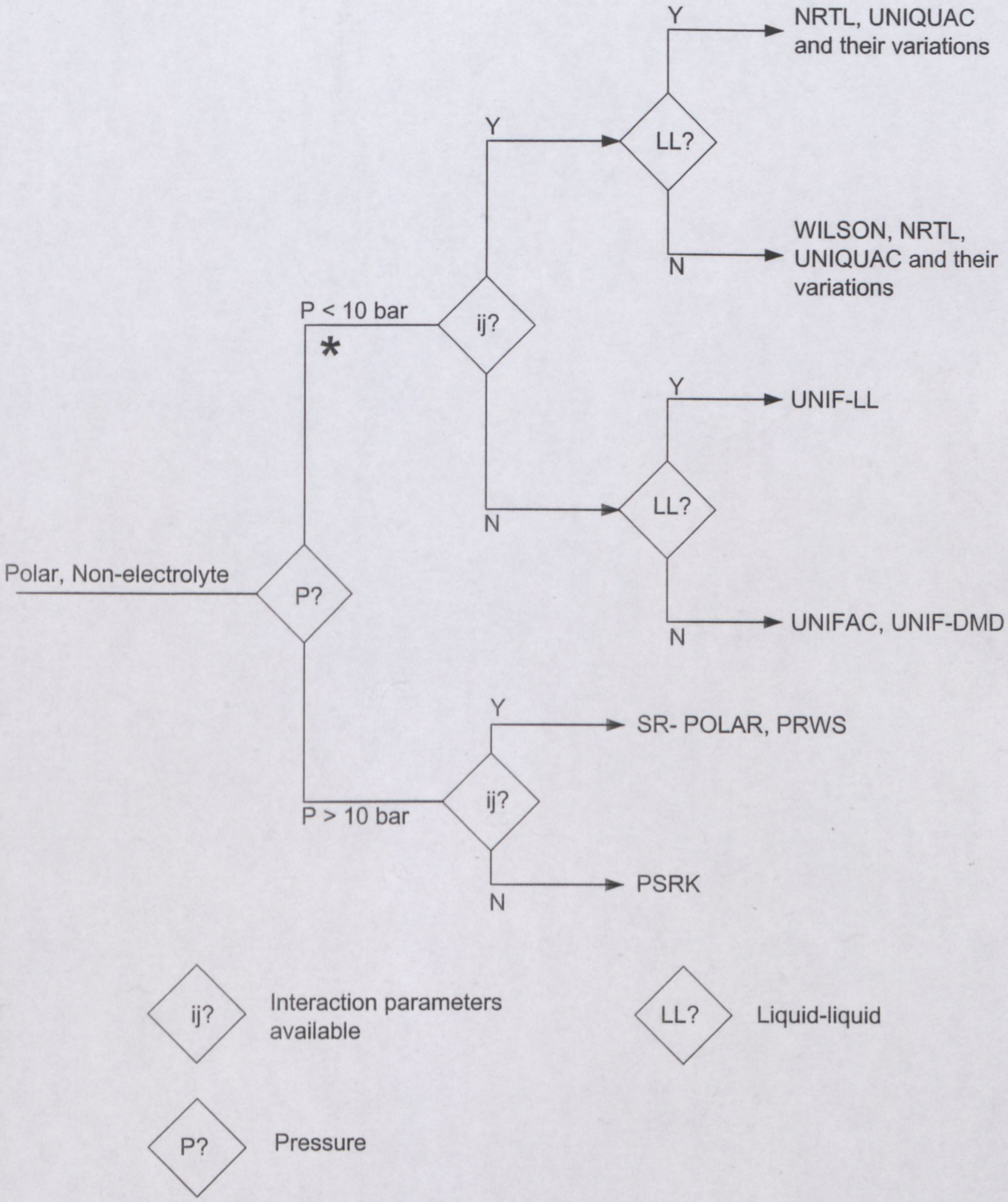
The choice of the property method depends on the degree of non-ideality and the operating conditions of the system.

The Aspen Plus simulation package supplies some guidelines when choosing a property method and is shown below:

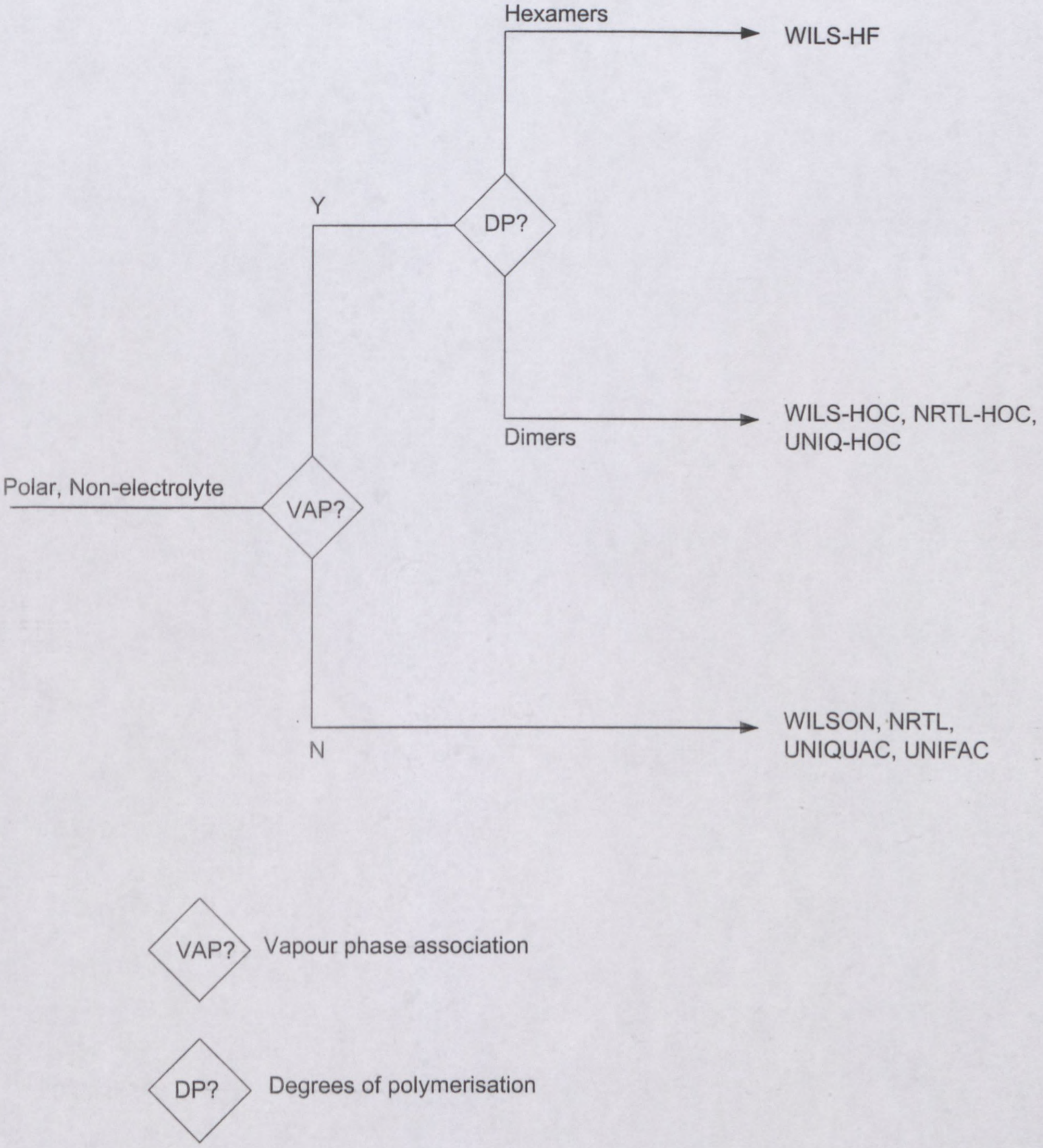
## Guidelines for choosing a property method [7].



* See next diagram to continue



* See next diagram to continue


Hexamers
WILS-HF
Y
DP?
Dimers
WILS-HOC, NRTL-HOC,
UNIQ-HOC
Polar, Non-electrolyte
VAP?
N
WILSON, NRTL,
UNIQUAC, UNIFAC
VAP?
Vapour phase association
DP?
Degrees of polymerisation

The property method that was selected for the simulation was UNIFAC. The reasons for the selection are:

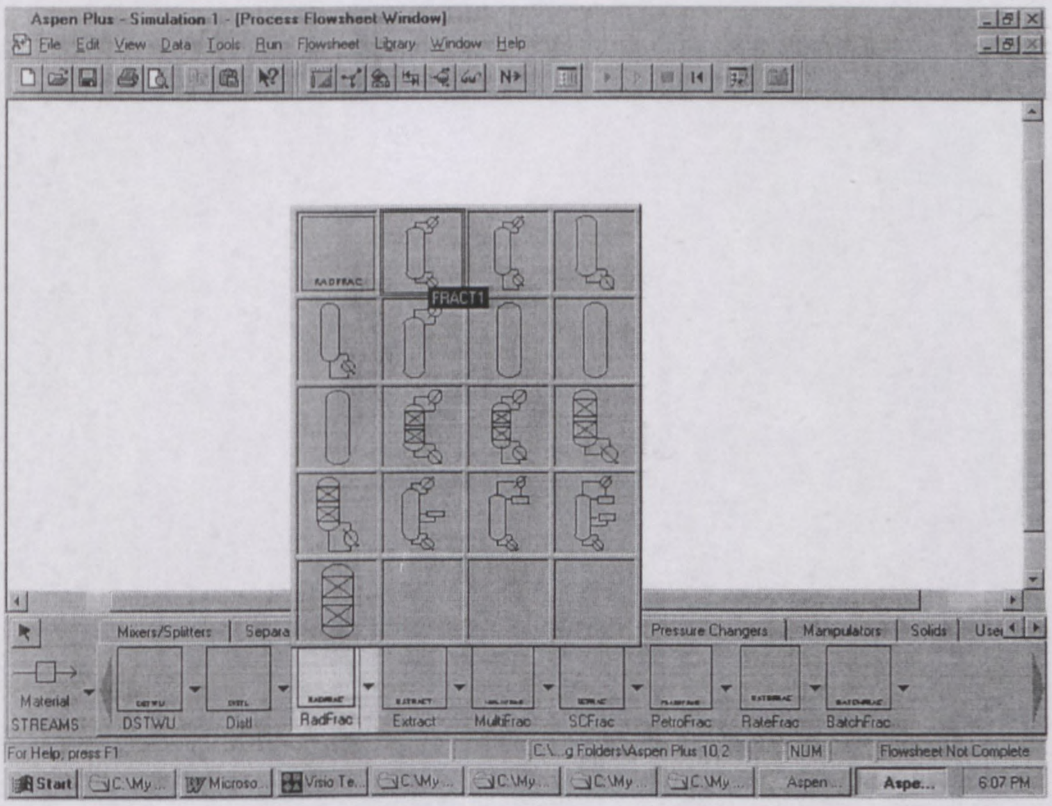
1. The system is polar.
2. The system is a non-electrolyte system.
3. The operating pressure of the system is less than 10 bar.
4. Interaction parameters between certain components are not available in the literature.
5. It is a vapour-liquid system.

## 5.2 Simulation set-up

The simulation set-up will be described chronologically according to the required inputs of the simulation engine.

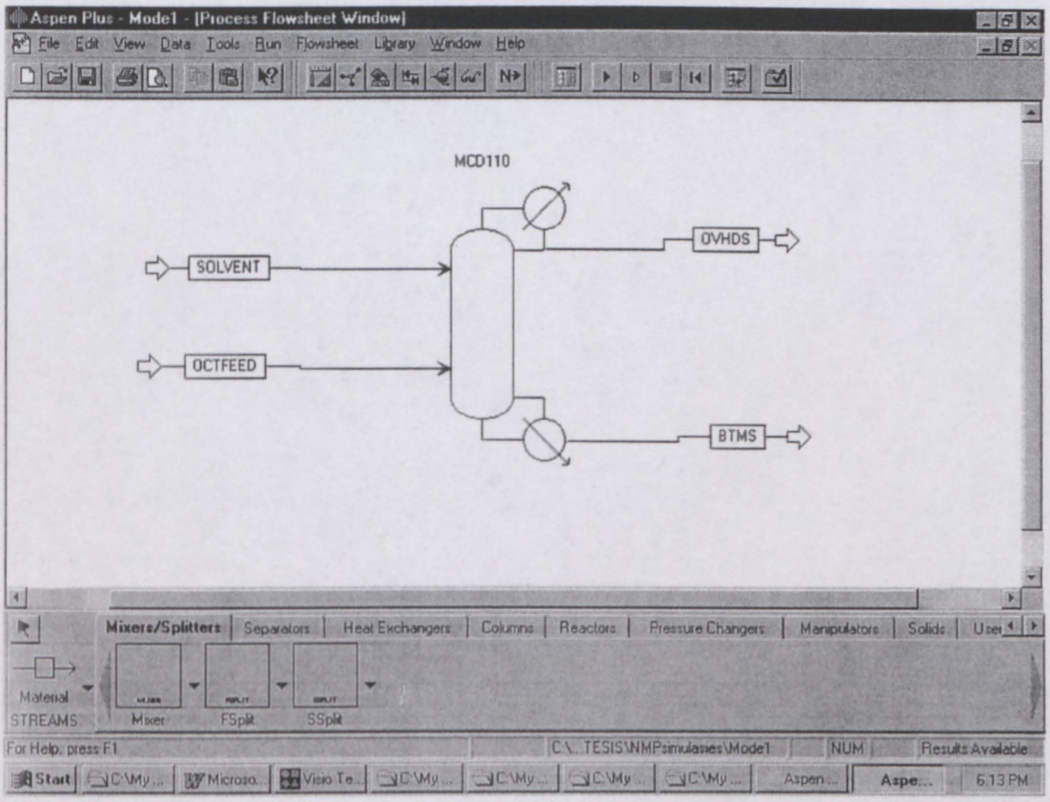
### 5.2.1 Distillation column selection

A FRACT1 distillation column was selected from the RADFRAC group, under the "column" icon in the Model library.



### 5.2.2 Completing the flowsheet

The flowsheet was completed by adding the required streams and connecting them to the respective points on the distillation column.



### 5.2.3 Completing the required inputs.

The following operating conditions and properties of the distillation column were included in the simulation.

#### 5.2.3.1 Operating pressure and column pressure drop

Operating pressure of 40 kPa abs and a column pressure drop of 2 kPa (obtained from piloting and packing vendor).

#### 5.2.3.2 Amount of theoretical stages and location of the feed streams

From the calibration of the distillation column, it is known that the column has 80 theoretical stages, numbering from the top, including the condenser. However, during extractive distillation, the amount of theoretical stages is less due to the high liquid loading in the column. The liquid loading in an extractive distillation column is much higher than during conventional distillation due to the fact that a high-boiling solvent is introduced at the top of the column and the ratio of the solvent to the feed is very high (25 : 1). The high liquid loading decreases the efficiency of the packing by approximately half.

Thus, the extractive distillation column has approximately 40 theoretical stages, numbering from the top, including the condenser. The solvent feed is located above stage 10 and the 1-octene feed is located above stage 32.

#### 5.2.3.3 Reflux- and distillate rate

The reflux- and distillate rates were entered according to the conditions of the pilot plant.

#### 5.2.3.4 Sub-cooled temperature of the condenser

From the piloting it is known that the condenser sub-cooled the reflux to 25°C.

#### 5.2.3.5 Octene recovery

The 1-octene recovery of the respective mode was entered in the "design specs" folder. In order to meet the design specification, a control parameter has to be selected and specified in the "vary" folder that can be varied in order to meet the design specification. In this case the distillate rate was the parameter that was selected in the "vary" folder.

#### 5.2.3.6 Rate, temperature and pressure of the two feed streams

The conditions of the feed streams were entered according to the conditions of the pilot plant.

#### 5.2.3.7 Property method

The property method selected for all the simulations was UNIFAC.

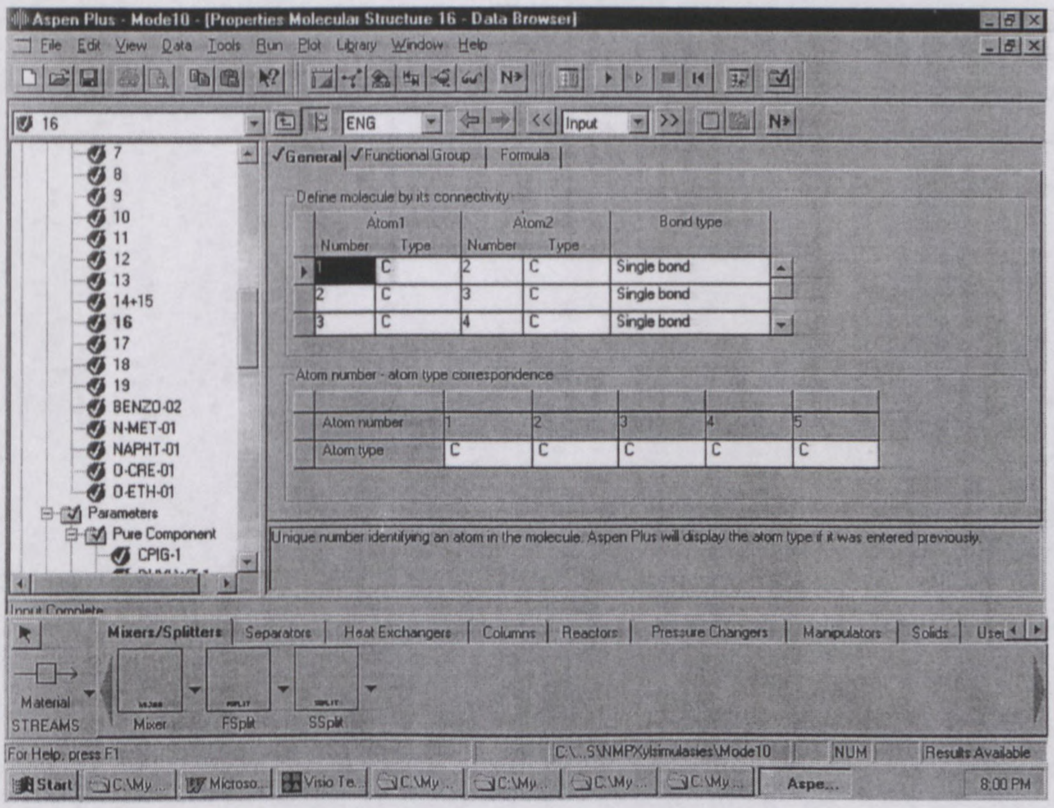
#### 5.2.3.8 Composition of the two feed streams

Not all the components in the different feed streams were available in the databases of the simulation engine. Thus, these components had to be "built" into the simulation and the boiling points were specified. The components that had to be built were:

- 2-ethyl-1-methylcyclopentene (component 8)
- 1,7-octadiene (component 10)
- 1,2,3-trimethylcyclopentene (component 12)
- 3-propyl-1,4-pentadiene (component 13)
- 6-methyl-1,5-heptadiene (component 14+15)
- isopropyl-cyclopentene (component 16)
- 4-methyl-1,6-heptadiene (component 17)
- 3-octyne (component 18)
- 2-octyne (component 19)

The process to build a component:

1. Name the component in "component" folder, in the "specifications" icon.
2. The molecular structure of the component must be supplied in the "molecular structure" sub-folder, in the "properties" folder.
3. Add the molecular structure by specifying the atom type, bond type, and functional group.



Define molecule by its connectivity

| Atom1 |  | Atom2 |  | Bond type |
|---|---|---|---|---|
| Number | Type | Number | Type |  |
| 1 | C | 2 | C | Single bond |
| 2 | C | 3 | C | Single bond |
| 3 | C | 4 | C | Single bond |

Atom number - atom type correspondence

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| Atom number | 1 | 2 | 3 | 4 | 5 |
| Atom type | C | C | C | C | C |

Unique number identifying an atom in the molecule. Aspen Plus will display the atom type if it was entered previously.

4. Specify the boiling point of the component under the “PURE-1” icon, in the “parameter” sub-folder, which is in the “molecular structure” folder.
5. The simulation engine requested the critical pressure of ethyl phenol as well. The critical pressure is also specified in the “PURE-1” icon, in the “parameter” sub-folder, which is in the “molecular structure” folder. “PC” must be selected from the drop-down list, in the parameter table.

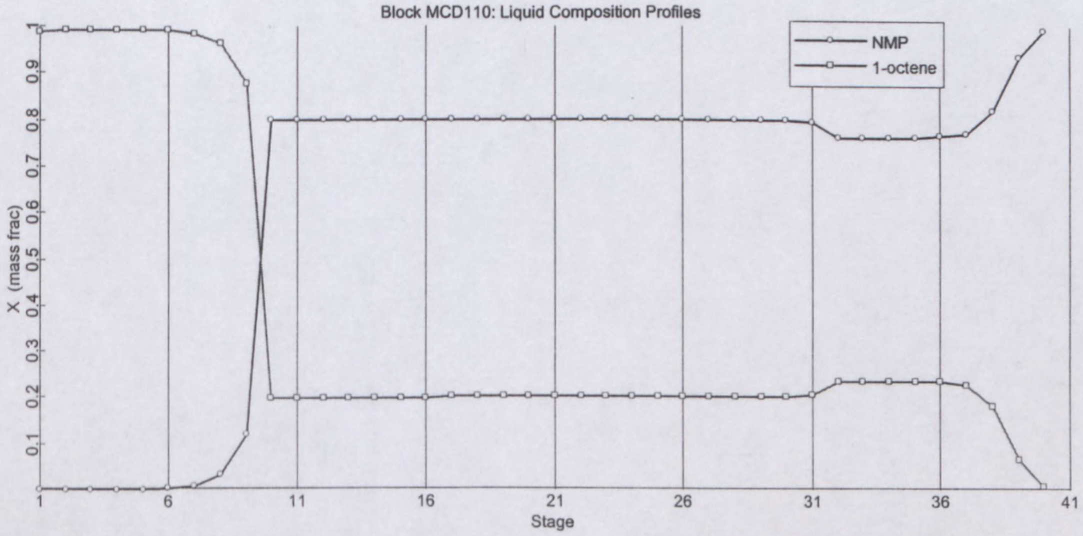
## 5.3 Simulation results

The overheads-composition results of all the different modes, predicted by the simulation are shown in Table 5. To illustrate the predictions of the simulation, the concentration-profiles of all the components were plotted against the different modes (figure 5h). The concentration-profiles of the impurities and the key components were also plotted and compared against the initial feed concentration.

Figure 5a illustrates the prediction of the extraction of component 2a+b+c. The simulation predicted a complete removal of the component.

Figure 5b compares the predicted 1-octene concentration-profile to the initial feed concentration. The simulation predicted that NMP performed better than xylenol as well as the NMP/xylenol mixture (mode 1 vs. mode 7 vs. mode 11, which were conducted at the same conditions).

The graph below indicates the typical liquid-concentration-profile of 1-octene throughout the extractive distillation column. The liquid concentration-profile of the solvent is included as well. In this case the solvent is NMP, which was used during mode 1.



From figure 5c it is clear that the concentration of component 5 increased compared to the initial feed concentration. The simulation predicted the same pattern for component 12 in figure 5e.

The simulation also predicted the complete removal of components 11 and 18, seen in figures 5d and 5g respectively.

The simulation predicted an interesting concentration-profile for component 14+15, illustrated in figure 5f. The simulation predicted that the NMP/xylenol mixture extracted the component completely, while the NMP extracted the component significantly and the xylenol did not extract the component at all.

Table 5 : Overheads composition results predicted by the simulation

| | Mode 1 | Mode 2 | Mode 3 | Mode 4 | Mode 5 | Mode 6 | Mode 7 | Mode 8 | Mode 9 | Mode 10 | Mode 11 | Mode 12 | Mode 13 | Mode 14 | Mode 15 | Mode 16 | Mode 17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **N-MET-01** | 4.12E-13 | 0 | 0 | 1.34E-13 | 0 | 0 | 0 | 0 | 0 | 9.64E-14 | 1.17E-13 | 9.75E-15 | 0 | 0 | 0 | 0 | 0 |
| **1** | 0.0005 | 0.00057 | 0.00055 | 0.00051 | 0.00074 | 0.00082 | 0.00079 | 0.00068 | 0.00079 | 0.00082 | 0.00079 | 0.00079 | 0.00067 | 0.00069 | 0.00069 | 0.00067 | 0.0007 |
| **2ABC** | 2.44E-21 | 2.21E-14 | 1.99E-15 | 5.27E-23 | 6.97E-13 | 1.88E-13 | 3.87E-14 | 1.66E-13 | 4.59E-12 | 1.58E-22 | 1.18E-22 | 4.96E-23 | 5.09E-11 | 1.08E-07 | 8.74E-13 | 2.42E-12 | 3.95E-12 |
| **3** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **4** | 0.98642 | 0.98362 | 0.98412 | 0.98777 | 0.98424 | 0.98279 | 0.98324 | 0.98539 | 0.98306 | 0.98564 | 0.98604 | 0.98602 | 0.9852 | 0.98483 | 0.98502 | 0.98536 | 0.98481 |
| **5** | 0.00379 | 0.00432 | 0.00413 | 0.00384 | 0.00419 | 0.00465 | 0.00445 | 0.00382 | 0.00448 | 0.00464 | 0.0045 | 0.00451 | 0.00381 | 0.00389 | 0.00388 | 0.00377 | 0.00394 |
| **6** | 0.00045 | 0.00041 | 0.00039 | 0.00038 | 0.00055 | 0.00054 | 0.00052 | 0.00055 | 0.00054 | 0.00043 | 0.00045 | 0.00041 | 0.00056 | 0.00056 | 0.00055 | 0.00056 | 0.00055 |
| **7** | 7.17E-05 | 6.68E-05 | 5.61E-05 | 5.78E-05 | 0.00012 | 0.00011 | 0.0001 | 0.00012 | 0.00011 | 6.89E-05 | 7.76E-05 | 5.90E-05 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 |
| **8** | 2.58E-12 | 4.90E-06 | 7.48E-06 | 6.01E-14 | 2.45E-05 | 1.39E-05 | 1.04E-05 | 2.19E-05 | 8.93E-05 | 3.70E-13 | 2.17E-13 | 1.02E-12 | 0.00015 | 0.00021 | 0.00012 | 0.00014 | 0.00013 |
| **9** | 2.53E-35 | 3.53E-35 | 1.46E-35 | 6.88E-35 | 2.51E-35 | 6.04E-35 | 6.22E-35 | 3.17E-35 | 9.70E-35 | 3.61E-35 | 2.35E-35 | 9.86E-35 | 1.31E-35 | 1.30E-35 | 9.87E-35 | 3.12E-35 | 6.04E-35 |
| **10** | 0.00034 | 0.00039 | 0.00037 | 0.00035 | 0.00033 | 0.00037 | 0.00035 | 0.0003 | 0.00036 | 0.00037 | 0.00036 | 0.00036 | 0.0003 | 0.00031 | 0.00031 | 0.0003 | 0.00031 |
| **11** | 5.71E-16 | 2.21E-11 | 1.58E-12 | 6.62E-20 | 8.89E-10 | 2.45E-10 | 3.44E-11 | 1.43E-10 | 4.72E-09 | 1.82E-19 | 1.42E-19 | 5.90E-20 | 4.98E-08 | 3.04E-05 | 7.54E-10 | 2.30E-09 | 4.22E-09 |
| **12** | 0.00642 | 0.00733 | 0.007 | 0.00648 | 0.00655 | 0.00726 | 0.00694 | 0.00596 | 0.00699 | 0.00723 | 0.007 | 0.00704 | 0.00595 | 0.00607 | 0.00606 | 0.00589 | 0.00615 |
| **13** | 7.29E-20 | 6.08E-13 | 1.03E-12 | 2.09E-22 | 4.06E-12 | 1.68E-12 | 1.93E-12 | 4.60E-12 | 8.97E-11 | 3.80E-21 | 1.55E-21 | 9.05E-21 | 4.77E-10 | 1.64E-08 | 1.39E-10 | 2.12E-10 | 2.15E-10 |
| **14+15** | 0.00135 | 0.0033 | 0.00338 | 8.08E-07 | 0.00323 | 0.00343 | 0.00359 | 0.00315 | 0.00354 | 5.88E-06 | 3.17E-06 | 1.72E-05 | 0.00313 | 0.00309 | 0.00322 | 0.00313 | 0.00322 |
| **16** | 2.70E-23 | 3.32E-16 | 2.27E-16 | 7.34E-26 | 1.02E-14 | 3.69E-15 | 3.33E-15 | 9.50E-15 | 1.91E-13 | 3.52E-24 | 1.54E-24 | 4.02E-24 | 1.26E-12 | 9.33E-11 | 1.80E-13 | 3.09E-13 | 3.28E-13 |
| **17** | 2.27E-17 | 3.37E-13 | 3.89E-13 | 3.55E-22 | 3.01E-12 | 1.19E-12 | 1.32E-12 | 3.38E-12 | 6.47E-11 | 7.15E-21 | 3.04E-21 | 1.19E-20 | 3.68E-10 | 1.37E-08 | 8.51E-11 | 1.36E-10 | 1.38E-10 |
| **18** | 0.0006 | 1.96E-06 | 1.56E-06 | 0.00058 | 1.66E-05 | 9.01E-06 | 2.62E-06 | 5.67E-06 | 4.88E-05 | 0.00077 | 0.00074 | 0.00076 | 9.93E-05 | 0.0002 | 4.16E-05 | 6.27E-05 | 7.27E-05 |
| **19** | 5.65E-05 | 4.56E-10 | 2.34E-10 | 3.12E-05 | 8.32E-09 | 3.68E-09 | 4.64E-10 | 1.02E-09 | 3.99E-08 | 3.29E-05 | 3.54E-05 | 3.68E-05 | 1.81E-07 | 7.54E-06 | 1.68E-08 | 4.11E-08 | 7.91E-08 |
| **NAPHT-01** | 0 | 1.61E-25 | 1.23E-26 | 4.52E-26 | 5.45E-25 | 3.22E-25 | 2.19E-25 | 4.84E-25 | 2.75E-25 | 2.89E-26 | 3.64E-26 | 2.68E-27 | 6.46E-25 | 2.06E-22 | 6.16E-26 | 7.90E-26 | 7.97E-26 |
| **BENZO-02** | 0 | 9.50E-27 | 6.80E-28 | 2.11E-27 | 3.39E-26 | 1.99E-26 | 1.26E-26 | 2.79E-26 | 1.64E-26 | 1.34E-27 | 1.69E-27 | 1.23E-28 | 3.88E-26 | 1.50E-23 | 3.48E-27 | 4.53E-27 | 4.66E-27 |
| **1-MET-01** | 0 | 1.28E-35 | 9.17E-35 | 3.52E-35 | 4.53E-35 | 2.66E-35 | 1.69E-35 | 3.76E-35 | 2.18E-35 | 2.17E-35 | 2.77E-35 | 1.98E-35 | 5.16E-35 | 1.94E-34 | 4.65E-35 | 6.06E-35 | 6.22E-35 |
| **2,6-X-01** | 0 | 1.01E-20 | 9.03E-22 | 4.34E-22 | 3.04E-20 | 1.84E-20 | 1.47E-20 | 3.16E-20 | 1.72E-20 | 3.19E-22 | 3.85E-22 | 3.31E-23 | 3.90E-20 | 7.93E-18 | 4.36E-21 | 5.38E-21 | 5.21E-21 |
| **O-ETH-01** | 0 | 1.15E-21 | 1.01E-22 | 4.99E-23 | 3.45E-21 | 2.09E-21 | 1.66E-21 | 3.57E-21 | 1.94E-21 | 3.67E-23 | 4.43E-23 | 3.79E-24 | 4.41E-21 | 9.07E-19 | 4.90E-22 | 6.05E-22 | 5.87E-22 |
| **2,5-X-01** | 0 | 1.65E-24 | 1.42E-25 | 6.75E-26 | 5.07E-24 | 3.06E-24 | 2.37E-24 | 5.10E-24 | 2.80E-24 | 4.91E-26 | 5.95E-26 | 5.04E-27 | 6.38E-24 | 1.41E-21 | 6.92E-25 | 8.60E-25 | 8.41E-25 |
| **2,4-X-01** | 0 | 1.60E-24 | 1.37E-25 | 6.31E-26 | 4.97E-24 | 2.99E-24 | 2.28E-24 | 4.93E-24 | 2.72E-24 | 4.56E-26 | 5.53E-26 | 4.67E-27 | 6.21E-24 | 1.41E-21 | 6.66E-25 | 8.31E-25 | 8.15E-25 |
| **O-CRE-01** | 0 | 2.98E-15 | 2.75E-16 | 1.18E-16 | 8.74E-15 | 5.32E-15 | 4.35E-15 | 9.29E-15 | 5.05E-15 | 8.81E-17 | 1.06E-16 | 9.34E-18 | 1.14E-14 | 2.08E-12 | 1.31E-15 | 1.61E-15 | 1.55E-15 |
| **3,5-X-01** | 0 | 1.53E-31 | 1.25E-32 | 5.49E-33 | 4.90E-31 | 2.94E-31 | 2.14E-31 | 4.64E-31 | 2.59E-31 | 3.88E-33 | 4.74E-33 | 3.95E-34 | 5.96E-31 | 1.51E-28 | 6.16E-32 | 7.76E-32 | 7.71E-32 |
| **SOLVENT** | 4.12E-13 | 2.98E-15 | 2.75E-16 | 1.34E-13 | 8.74E-15 | 5.32E-15 | 4.35E-15 | 9.29E-15 | 5.05E-15 | 9.65E-14 | 1.17E-13 | 9.76E-15 | 1.14E-14 | 2.08E-12 | 1.31E-15 | 1.61E-15 | 1.55E-15 |

**Figure 5a : Prediction of the extraction of component 2a+b+c by the simulation**

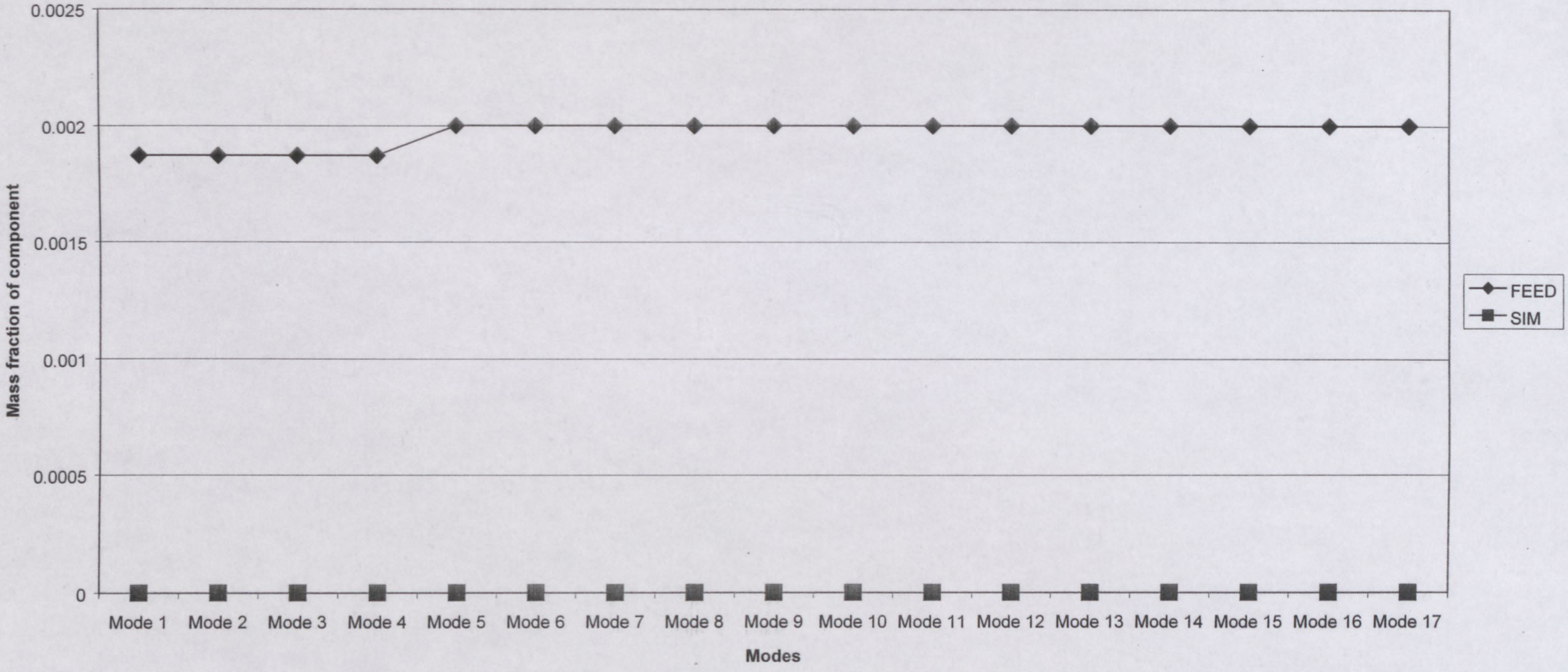


Figure 5b : Prediction of the concentration of 1-octene by the simulation

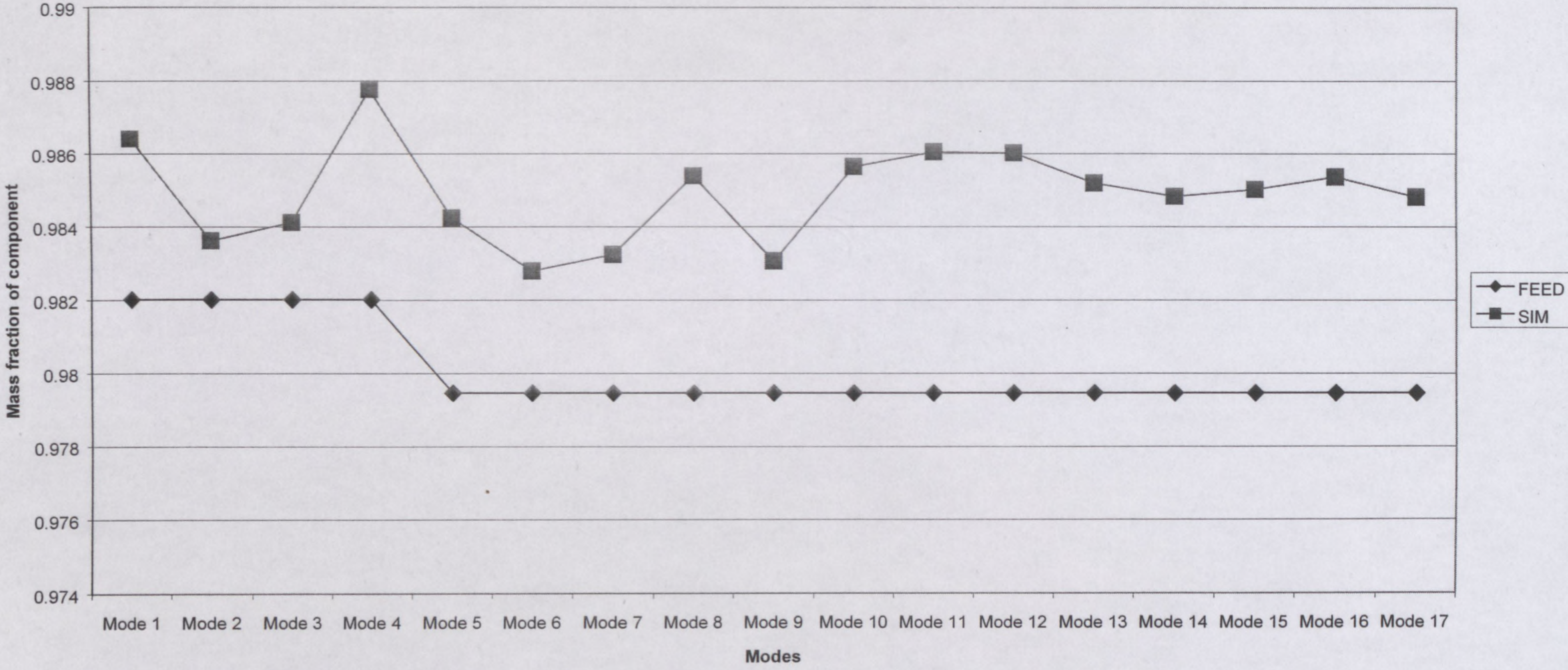


Figure 5c : Prediction of the extraction of component 5 by the simulation

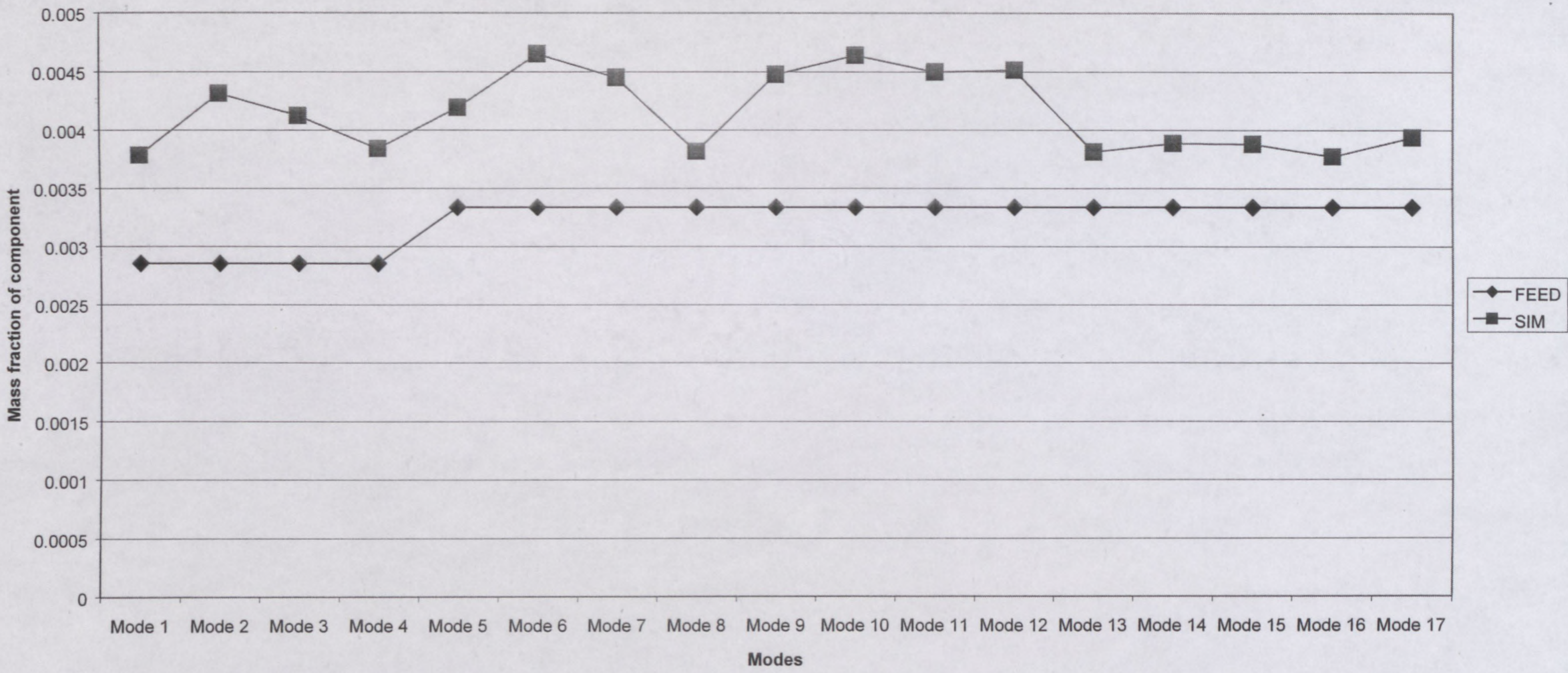


Figure 5d : Prediction of the extraction of component 11 by the simulation

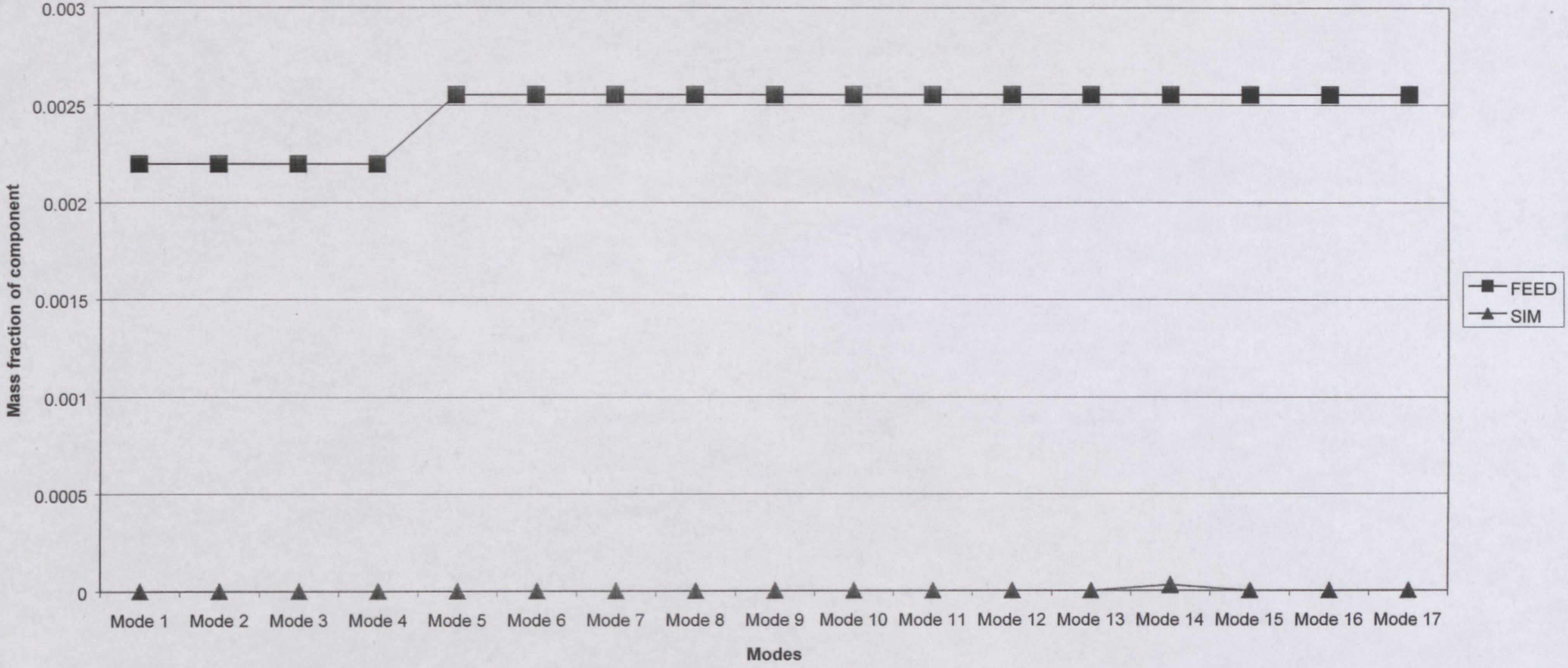


Figure 5e : Prediction of the extraction of component 12 by the simulation

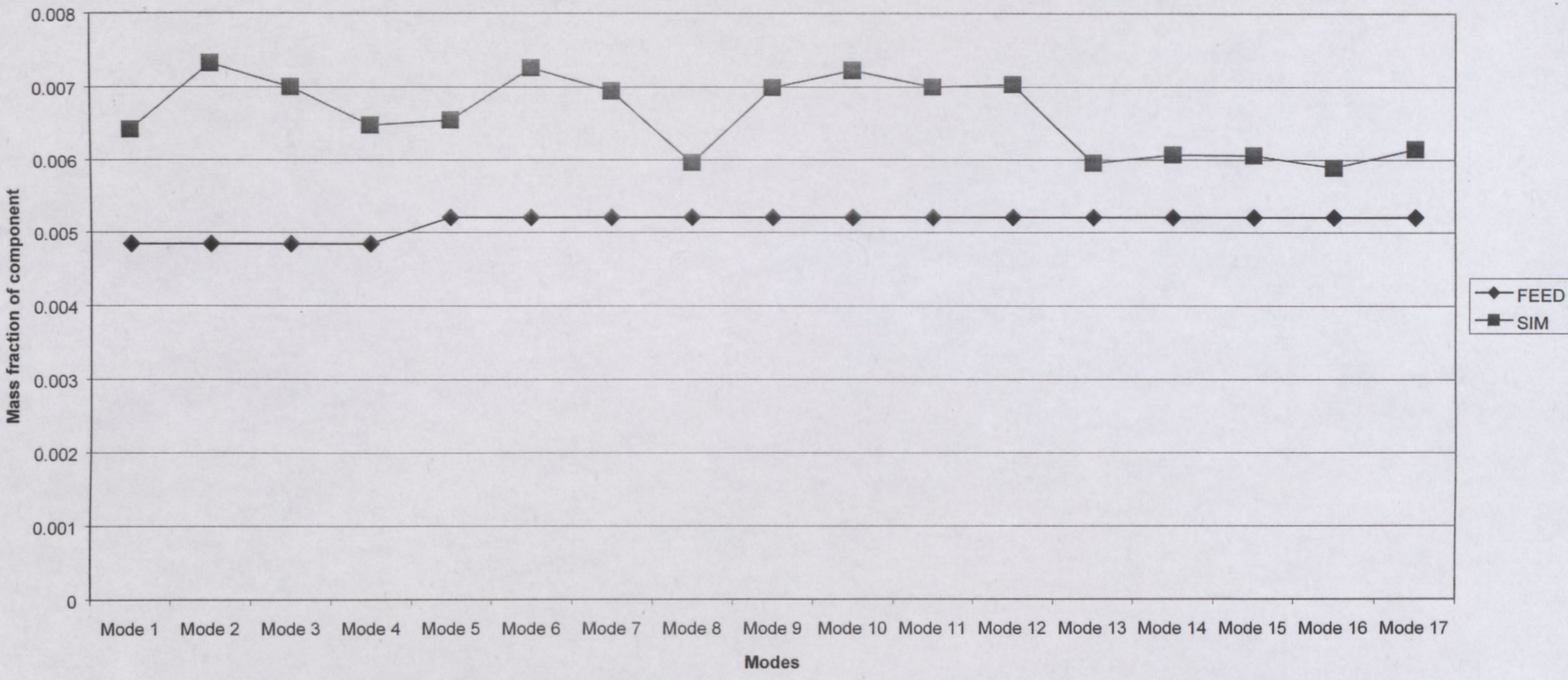


Figure 5f : Prediction of the extraction of component 14+15 by the simulation

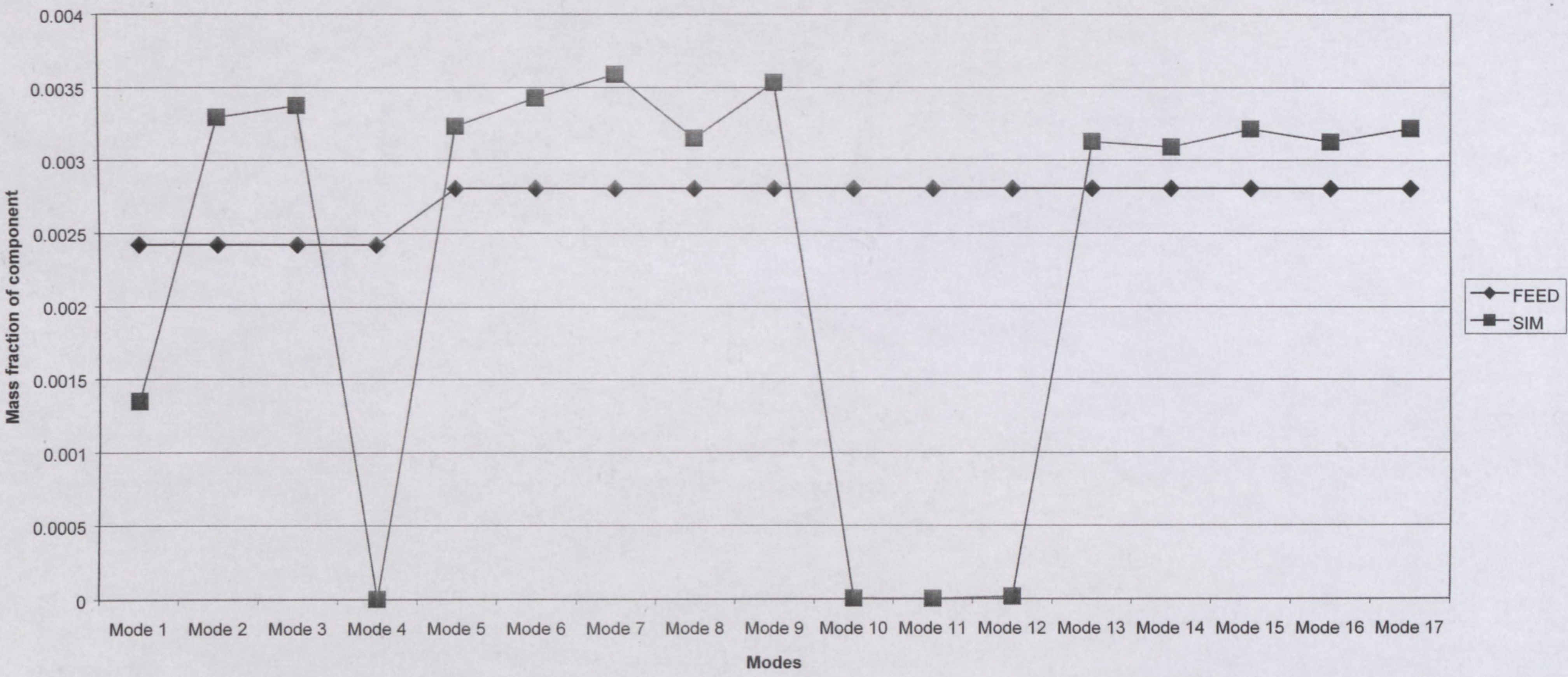


Figure 5g : Prediction of the extraction of component 18 by the simulation

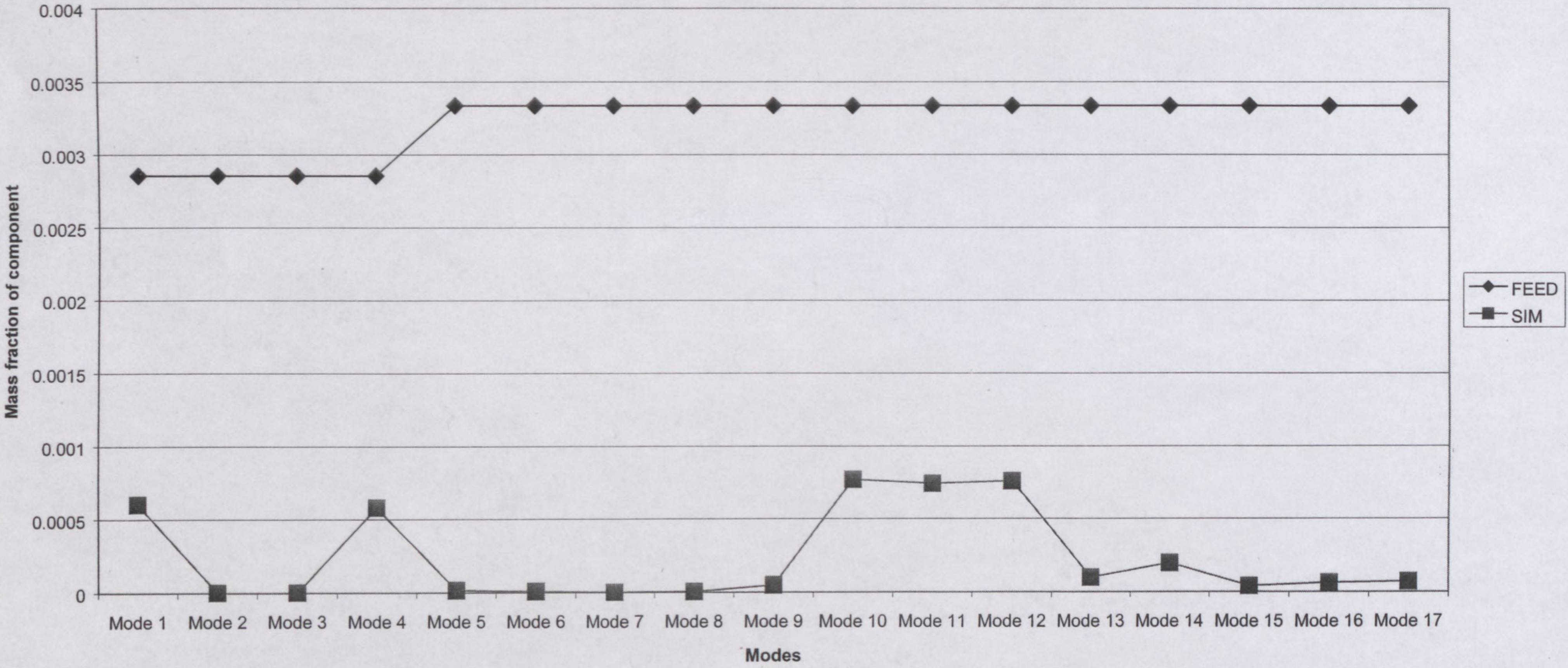
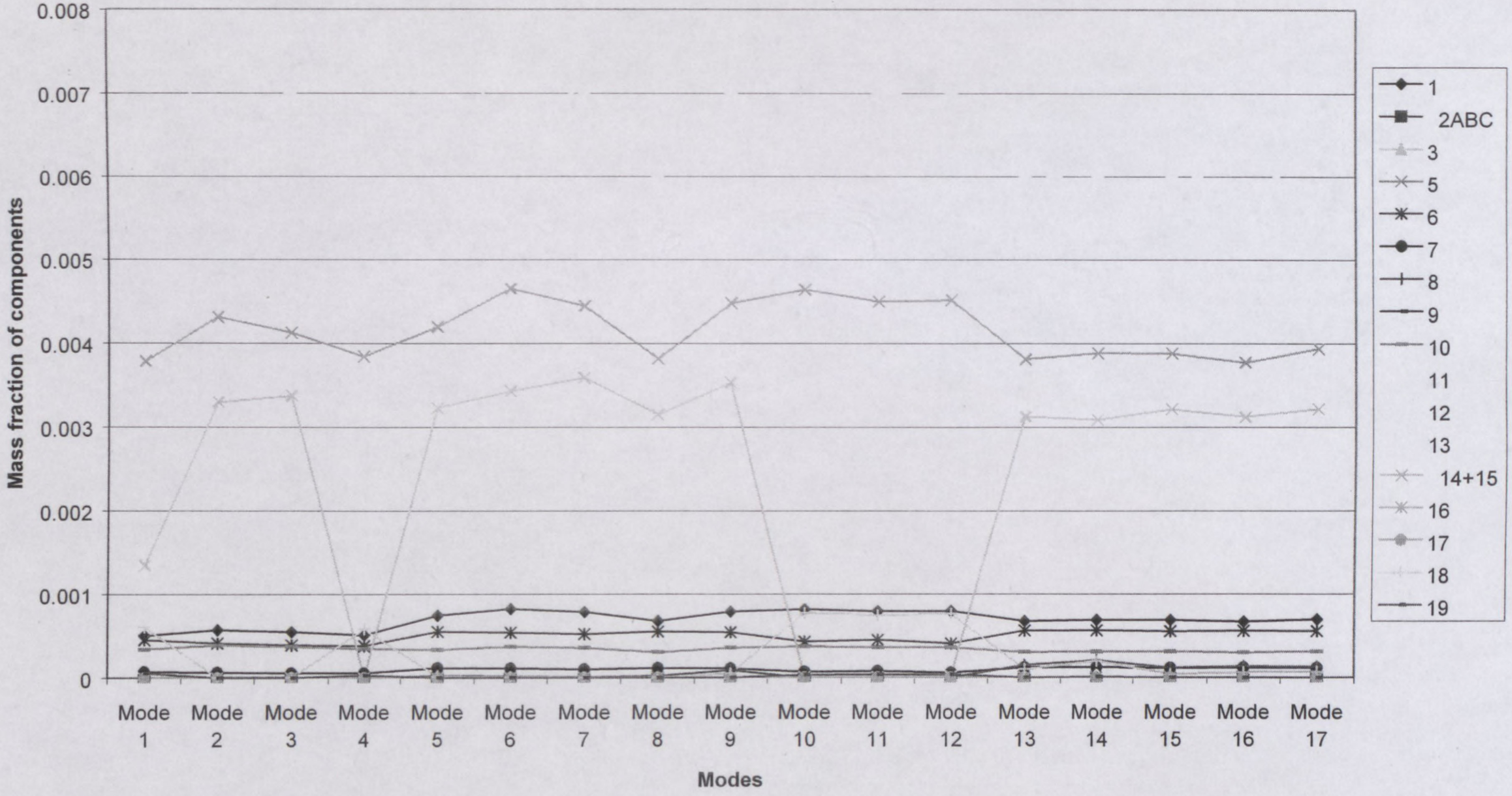


Figure 5h : Prediction of the extraction of all the components



# CHAPTER 6

# COMPARING THE PILOT PLANT RESULTS TO THE SIMULATION RESULTS

If the simulation results are compared to the pilot plant test work, a conservative prediction by the simulation is detected. Some differences are evident and are best explained by means of graphs.

To illustrate the differences between the simulation prediction and the pilot plant results, the concentration-profiles of the following components were plotted and are attached:

- Figure 6a : 1-methyl-1-ethyl-cyclopentane (component 2a+b+c)
- Figure 6b : 1-octene (component 4)
- Figure 6c : 2,3-dimethyl-1-hexene (component 5)
- Figure 6d : 2-ethyl-1-hexene (component 11)
- Figure 6e : 1,2,3-trimethyl-1-hexene (component 12)
- Figure 6f : 6-methyl-1,5-heptadiene (component 14+15)
- Figure 6g : 3-octyne (component 18)

**Figure 6a : 1-methyl-1-ethyl-cyclopentane (component 2a+b+c)**

From figure 6a, it is apparent that the simulation predicted the component 2a+b+c to be extracted completely, while the piloting proved an increase in concentration of component 2a+b+c (relative to the feed concentration). No definite pattern is observed between the concentration of component 2a+b+c and the different solvents used.

**Figure 6b : 1-octene (component 4)**

Figure 6b compares the 1-octene concentration-profile of the simulation prediction to the pilot plant results. The simulation predicted the same concentration profile, except for the following:

- During modes 2, 5, 6, 9 and 17 the simulation predicted a decrease in 1-octene concentration, while the piloting indicated an increase.

- During modes 3, 7 and 8 the simulation predicted an increase in 1-octene concentration, while the piloting indicated a decrease.

The concentration of the 1-octene predicted is on average 0.1 – 0.2% less than the pilot plant proved (modes 1,4, 10 – 17). During modes 2, 3, 5, 6, 7 and 9 the difference in concentration of 1-octene between the simulation-prediction and the piloting is approximately 0.4 – 0.5%.

The simulation predicted a sharp increase in 1-octene concentration from mode 3 to mode 4, while the piloting indicated only a slight increase. This deviation can be attributed to the simulation predicting better extraction.

Also, the simulation predicted a sharp decrease in 1-octene concentration from mode 8 to mode 9, while the piloting showed no major deviation. This deviation can be attributed to the change in 1-octene recovery. The simulation predicted a decrease in 1-octene concentration with a decrease in 1-octene recovery, while the piloting proved the opposite.

The simulation predicted that NMP performed better than xylenol as well as the NMP/xylenol mixture (mode 1 vs. mode 7 vs. mode 11). The pilot plant test work proved that xylenol performed better than the NMP/xylenol mixture as well as the NMP (mode 2 and 5 – 7).

**Figure 6c : 2,3-dimethyl-1-hexene (component 5)**

From figure 6c, it is clear that the simulation predicted no extraction of component 5 (the concentration increased compared to the feed concentration), while the piloting proved that the component was extracted. The simulation predicted the opposite concentration-profile for component 5 than what the pilot plant results showed. When the pilot-plant-concentration-profile of component 5 increased, the simulation predicted a decrease, and vice versa.

### Figure 6d : 2-ethyl-1-hexene (component 11)

Figure 6d shows a comparison between the simulation-prediction and the pilot plant test work. The simulation predicted a complete removal of component 11, while the pilot plant test work proved a significant reduction of component 11. Evaluating the pilot plant results, the xylenol definitely proved to be the better solvent (modes 2, 6 and 7).

### Figure 6e : 1,2,3-trimethyl-1-hexene (component 12)

Figure 6e compares the extraction of component 12 between the simulation prediction and the pilot plant test work. The simulation predicted no extraction of component 12 (the concentration increased compared to the feed concentration), while the piloting proved that the component was extracted significantly.

There is also a definite pattern between the two concentration profiles, i.e. the simulation predicted exactly the opposite than what the piloting proved. When the pilot-plant-concentration-profile of component 12 increased, the simulation predicted a decrease, and vice versa.

### Figure 6f : 6-methyl-1,5-heptadiene (component 14+15)

Figure 6f shows an interesting predicted concentration-profile of component 14+15. The simulation predicted that only the solvent mixture of NMP and xylenol completely removed component 14+15, while NMP extracted the component significantly and xylenol did not extract the component at all (the concentration of the component increased compared to the feed concentration).

The pilot plant results indicate the opposite pattern that was observed from the simulation prediction. The pilot plant results show a significant reduction in the concentration of component 14+15, compared to the initial feed concentration. The piloting proved that xylenol performed better than NMP as well as the NMP/xylenol mixture.

### Figure 6g : 3-octyne (component 18)

Figure 6g compares the extraction of component 18 between the simulation prediction and the pilot plant test work. The simulation predicted exactly the same concentration-profile of component 18 as the piloting proved. In both cases the component is significantly extracted.

A definite pattern is also noted, in that the concentration of component 18 increased in both cases when the solvent mixture of NMP and xylenol was used (modes 4, 10, 11 and 12).

Figure 6a : Comparing the extraction of component 2a+b+c between the simulation prediction and the pilot plant test work

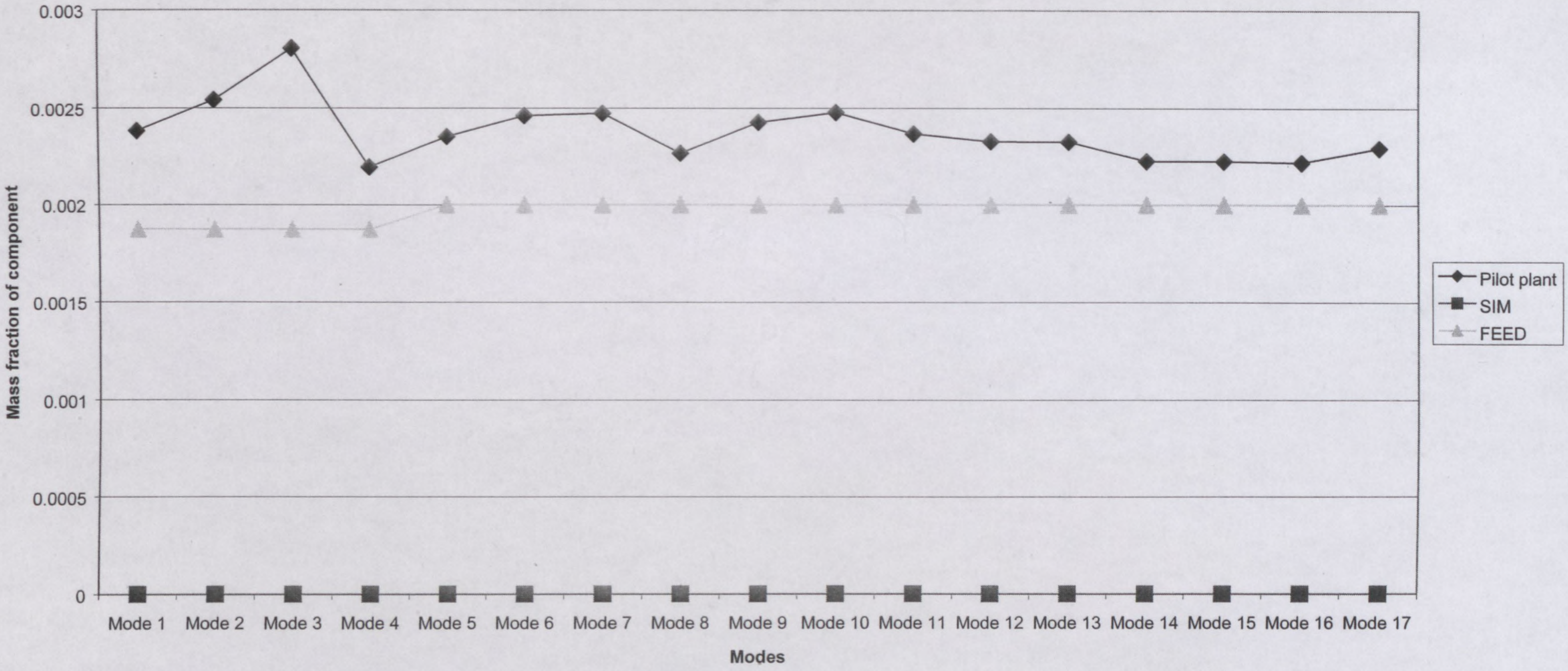


**Figure 6b : Comparing the concentration of 1-octene between the simulation prediction and the pilot plant test work**

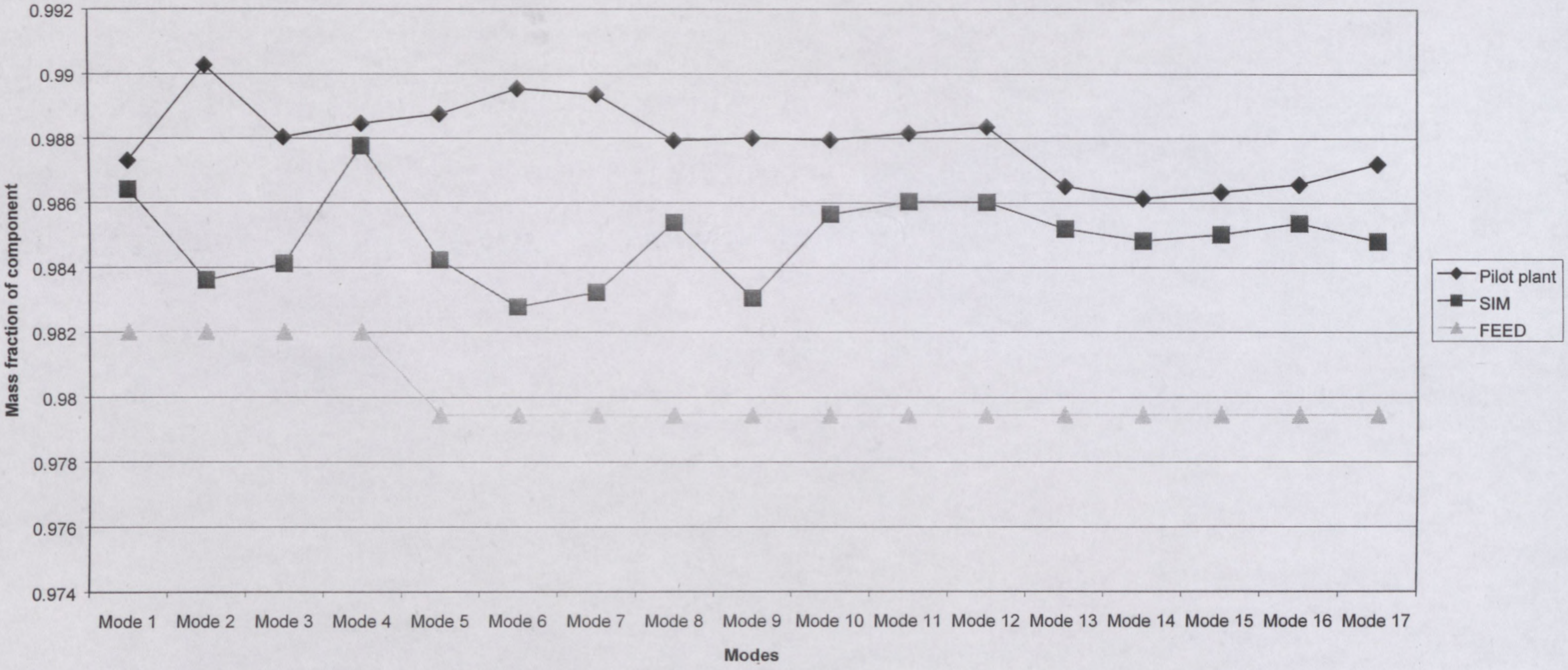


Figure 6c : Comparing the extraction of component 5 between the simulation prediction and the pilot plant test work

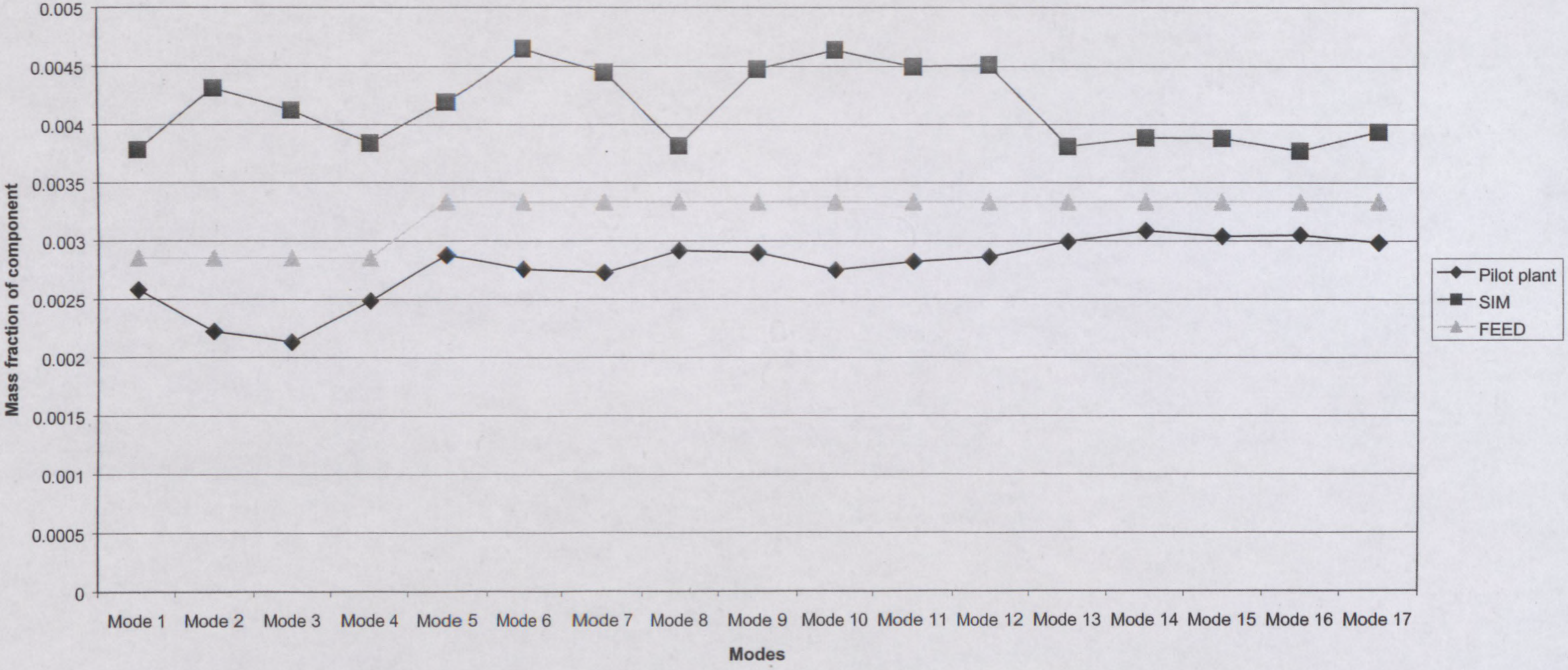


Figure 6d : Comparing the extraction of component 11 between the simulation prediction and the pilot plant test work

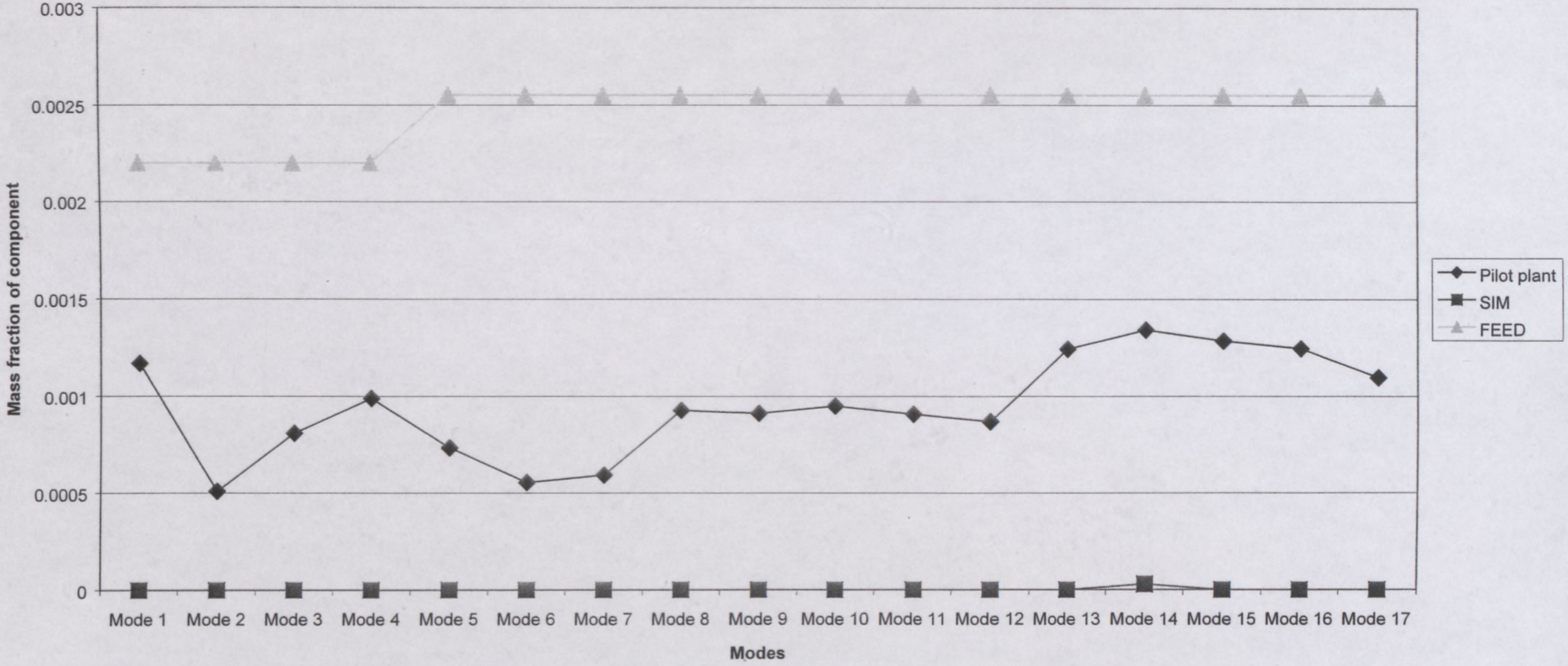


Figure 6e : Comparing the extraction of component 12 between the simulation prediction and the pilot plant test work

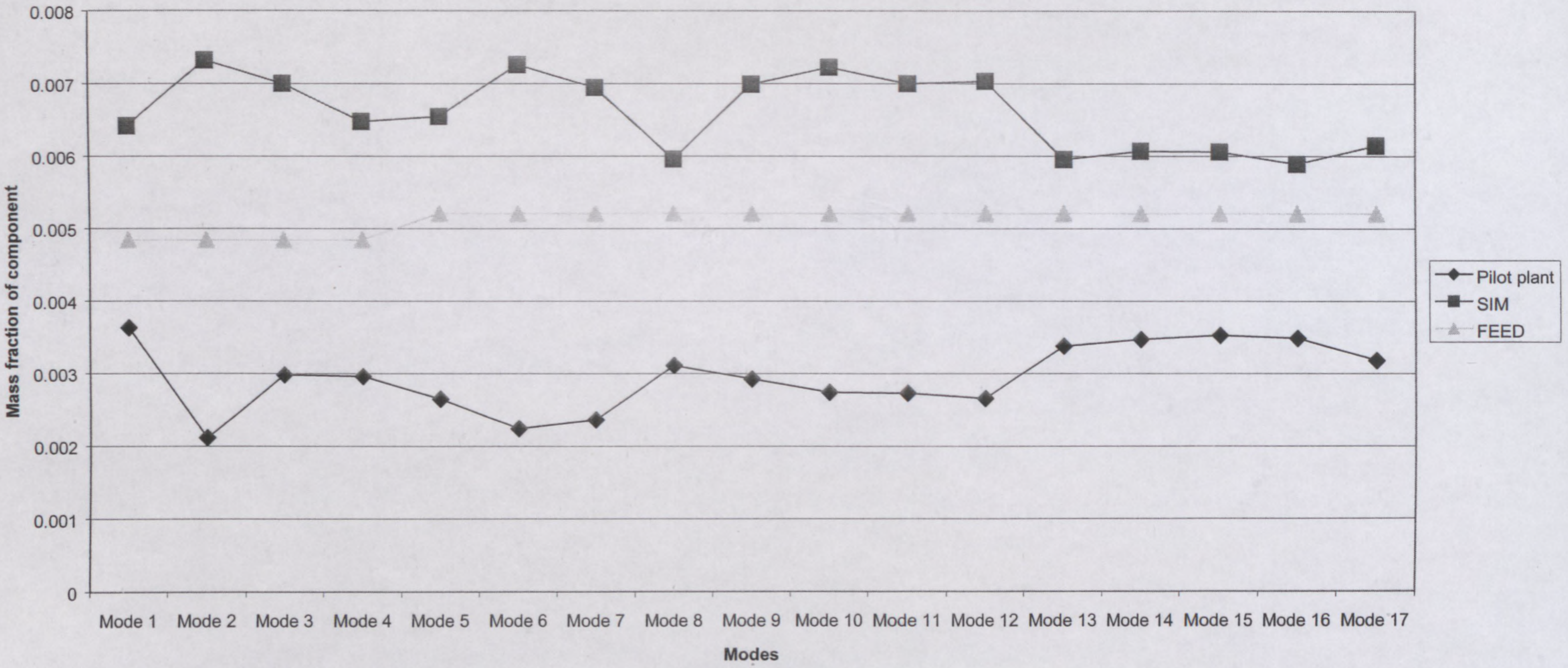


Figure 6f : Comparing the extraction of component 14+15 between the simulation prediction and the pilot plant test work

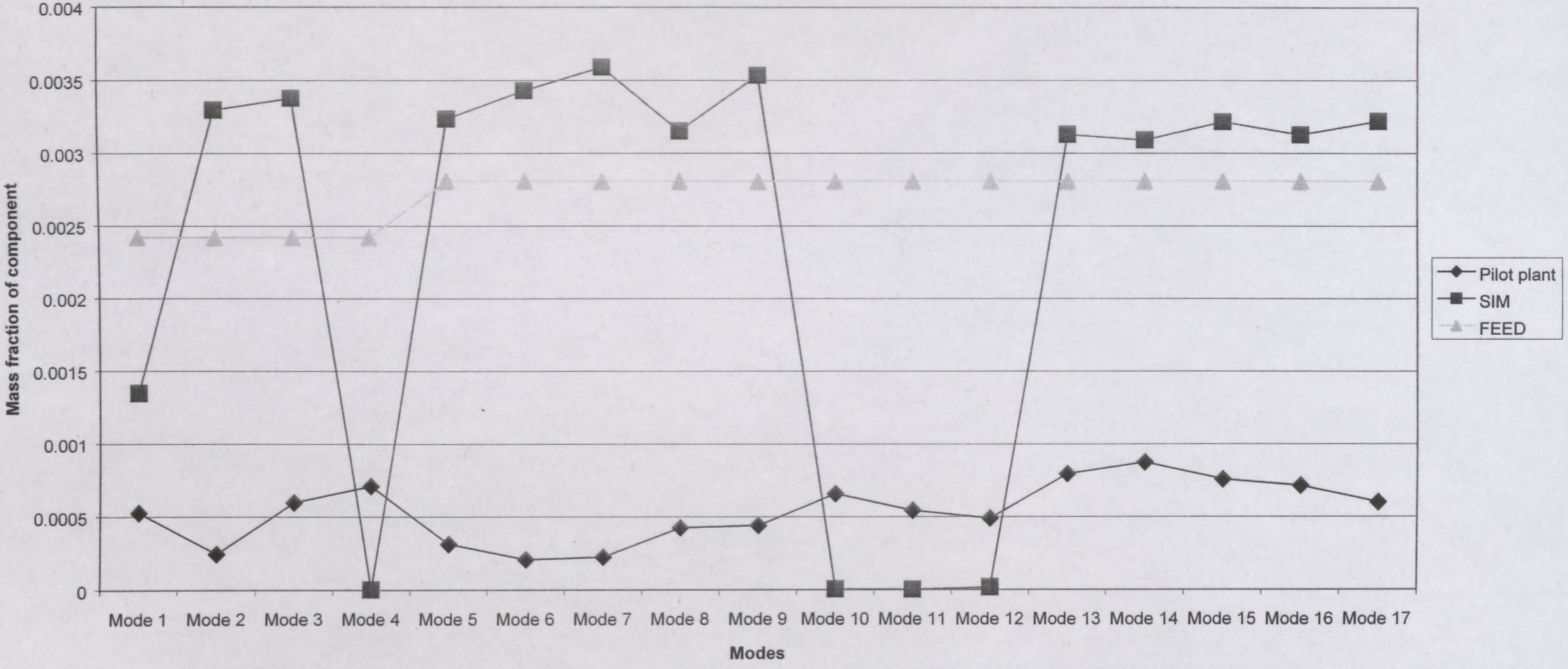
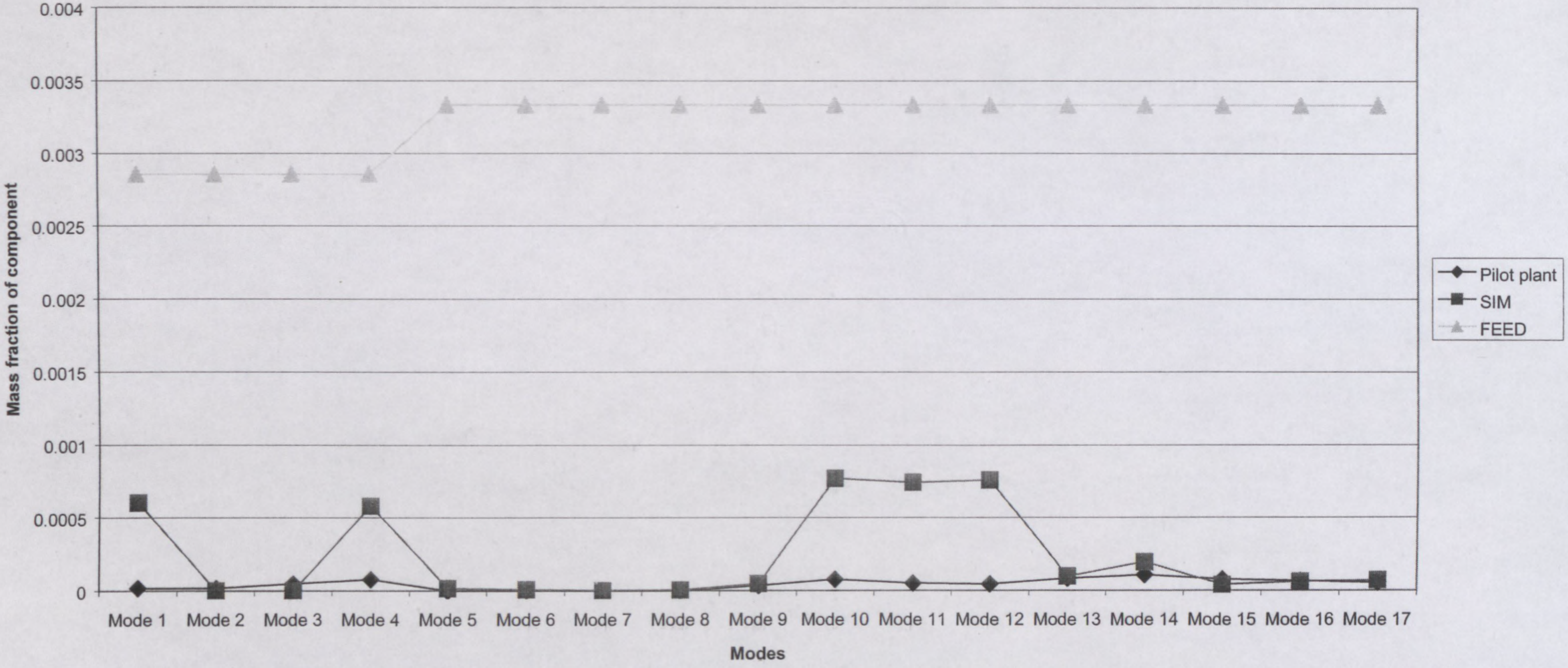


Figure 6g : Comparing the extraction of component 18 between the simulation prediction and the pilot plant test work



## 6.1 Discussion

The pilot plant test work proved that xylenol performed better than NMP as well as the NMP/xylenol mixture. The simulation predicted that NMP performed better than xylenol as well as the NMP/xylenol mixture.

In order to assess the repeatability of the simulation, as well as the accuracy of the simulation compared to the pilot plant results, an analysis of the extraction of the key components and the impurities has to be conducted.

**Evaluating component 2a+b+c**

From figure 6a, the simulation predicted the extraction of component 2a+b+c to be complete, irrespective of what solvent was used. Evaluating the pilot plant data for the same component, an increase in the concentration of the component relative to the feed concentration is observed, as opposed to the decrease predicted.

However, xylenol still proved to be the better solvent to remove the component to the smallest concentration (modes 8, 14, 15 and 16).

**Evaluating the extraction component 4**

The simulation-prediction approximates the concentration-profile of 1-octene, compared to the pilot plant test work. There are situations where the simulation-prediction and the piloting results do not correspond and the simulation proved to be inaccurate in predicting a change in 1-octene recovery.

From figure 6b, the simulation predicted that the NMP/xylenol mixture would be the better extraction solvent (modes 1 vs. mode 7 vs. mode 11). The pilot plant results proved that xylenol is the better extraction solvent (modes 2 and 5 – 7).

### Evaluating component 5

Figure 6c compares the concentration-profile of component 5 between the simulation-prediction and the pilot plant test work. The piloting results indicated that component 5 was extracted by the solvent, but not significantly. Although the simulation did not predict a decrease in concentration of component 5 relative to the feed concentration, it is observed that the simulation predicted exactly the opposite concentration profile, compared to the piloting results. The simulation predicted an increase in concentration, while the pilot plant results proved a decrease (modes 2, 6, 9 and 10) and vice versa (modes 4, 8, 11 and 13).

### Evaluating component 11

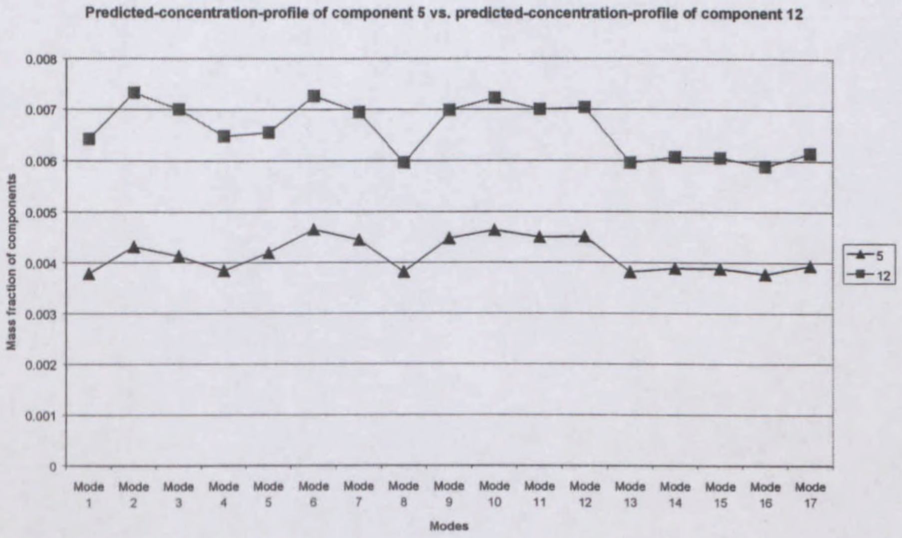
The simulation predicted a complete removal of component 11 (figure 6d), while the pilot plant tests proved that the component was extracted by approximately 50%. From the pilot plant data it was shown that xylenol performed better than the other solvents (mode 2, 6 and 7). The optimised conditions (modes 13 – 17) proved to be the worst performance of xylenol.

### Evaluating component 12

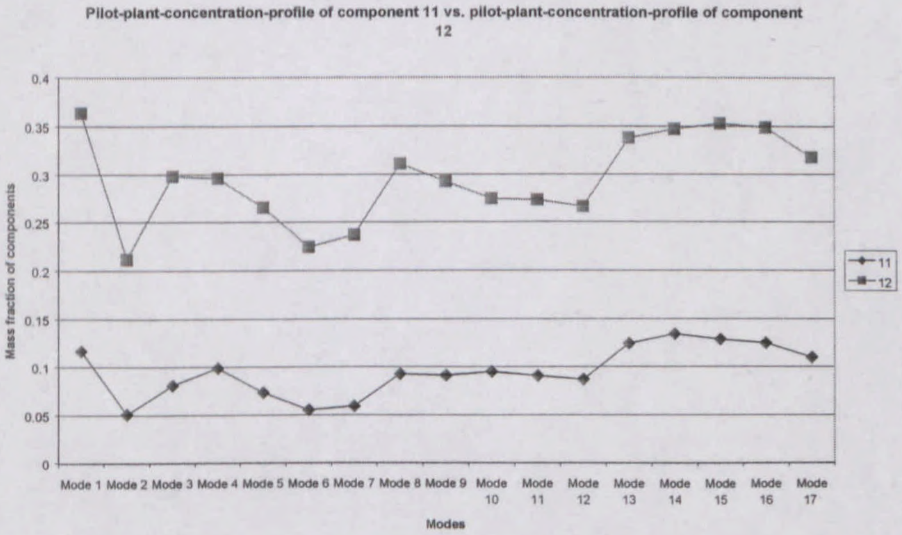
Figure 6e shows the same scenario as for component 5. The simulation predicted an increase in concentration of component 12 compared to the initial feed concentration, while the pilot plant tests proved that the component was extracted (about 50%). Again the simulation predicted the opposite concentration-profile of component 12, compared to the pilot plant results.

The pilot plant tests proved that xylenol is the better solvent in reducing the concentration of component 12 (modes 2, 6 and 7).

A very interesting observation is that the concentration-profile predicted by the simulation for component 12 is almost exactly the same profile predicted for component 5 (see graph below and figure 5h). Component 12 had to be "built" into the simulation, while component 5 was in the database.



Another very interesting observation, is that the pilot-plant-concentration-profile of component 12 is almost exactly the same as the pilot-plant-concentration-profile of component 11 (see graph below and figures 6d & e). Again the optimised conditions (modes 13 – 17) proved to be the worst performance of xylenol.

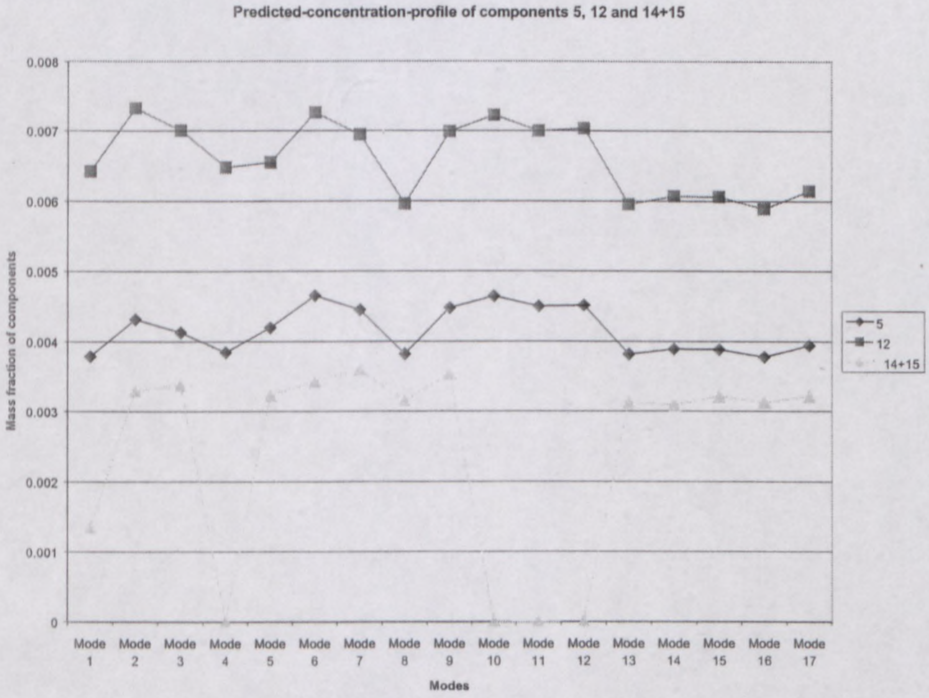


## Evaluating component 14+15

Figure 6f compares the concentration-profile of component 14+15 between the simulation prediction and the pilot plant test work. The simulation predicted that the NMP/xylenol mixture extracted the component completely, while NMP extracted the component about 50% and xylenol did not extract the component at all (the concentration increased relative to the initial feed concentration).

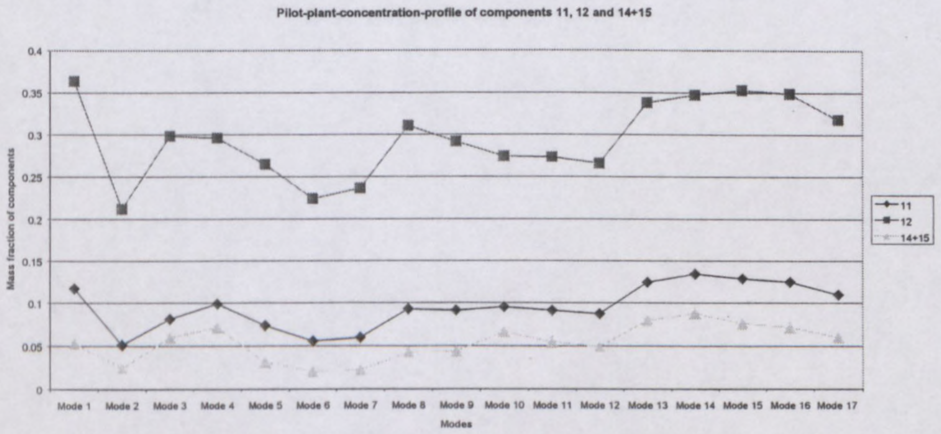
Again the pilot plant results proved an opposite concentration-profile of component 14+15, compared to the simulation-prediction.

If the simulation-predicted-concentration-profiles of components 5, 12 and 14+15 are plotted on one graph (see graph below), the similarity of the concentration-profiles for each component, except for component 14+15 at modes 4 and 10 – 12 is observed.



From figure 6f, the pilot plant tests proved that xylenol was the better solvent (modes 2, 6 and 7).

The trend of the pilot-plant-concentration-profile of component 14+15 during piloting is very much the same as for components 11 and 12 (see graph below). This is an indication that the pilot plant data is repeatable. However, it also indicates that the optimisation tests were not conducted at the optimum conditions. The reason is that the optimisation tests were done at a 1-octene recovery of 85%, the same as mode 8. From the graph below it is obvious that the extraction was better at mode 8.



## Evaluating component 18

Figure 6g shows that the simulation predicted almost exactly the same concentration-profile for component 18 as the pilot plant tests proved. Xylenol proved to be the better solvent.

# CHAPTER 7

# CONCLUSIONS and RECOMMENDATIONS

The best solvent proved to be xylenol. The NMP/xylenol mixture performed worse as an extraction solvent than xylenol, but was superior to NMP.

The best-extraction-solvent-optimisation tests that were conducted during the pilot plant test work (Modes 13 – 17) were in fact not done at the most optimised conditions. Figures 6b, d, e and f explain this statement. Mode 8 proved to be the most optimised condition. Further optimisation should be done on xylenol as well as the NMP/xylenol mixture.

The simulation predicted that NMP would be the better solvent, which is inaccurate. The 1-octene concentration-profile predicted by the simulation is comparable to the pilot-plant-concentration-profile, except for a few conditions. The simulation is also inaccurate in predicting a change in 1-octene recovery.

The simulation is inaccurate in predicting the concentration-profiles of the following components:

- Component 2a+b+c
- Component 5
- Component 11
- Component 12
- Component 14+15

Components 12 and 14+15 were "built" into the simulation. Thus, the lack of accurate physical-property-data and VLE-data is a reason given why the simulation-prediction is inaccurate.

The UNIFAC property method that was used in the simulation is an activity model based on group contributions, which makes the model predictive. It is a predictive method of calculating phase equilibria, and therefor, it should be used only in the absence of experimental information, as in this case. The UNIFAC method yields fairly accurate predictions, but it becomes less reliable in the dilute regions, especially for highly non-ideal systems [8].

There are shortcomings of the UNIFAC method when a component has to be "built" into the simulation:

- If the component to be "built" has a functional group (ethyl, methyl, propyl, etc.), the exact location of the functional group cannot be specified. Only the number of occurrences can be specified. For example, the model will not distinguish between 4-methyl-2-heptene and 2-methyl-2-heptene. Thus, the model can not distinguish between different isomers.
- Cyclic bonds can not be specified from the "bond type" drop-down list.

In order to overcome the shortcomings of the UNIFAC method, the boiling points of the "built" components were specified. Thus, the model cannot predict accurate phase equilibria for the "built" components, which is another reason why the simulation-prediction is inaccurate.

# CHAPTER 8

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# DECLARATION

I hereby certify that this thesis is my own original work, except for the acknowledgements in the text.

Himmel

E.A. HIMMELSTüTZER

November 2002