

# The effect of branched alcohol isomers on the separation of alkanes and alcohols with supercritical CO<sub>2</sub>

M. Zamudio, C.E. Schwarz, J.H. Knoetze\*

Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland, 7602, South Africa  
Tel: +27 21 8084488, Fax: +27 21 8082059, E-mail: jhk@sun.ac.za

Alcohols with hydrocarbon backbones of 8 to 20 carbon atoms are mainly used in the phthalate, detergent and surfactant industries. The majority of alcohol production processes lead to the formation of a variety of alcohol isomers. For further processing of the alcohols a post-production separation process is required to remove unconverted alkanes, and in certain cases, unconverted alkanes as well as alcohol isomers, from the primary linear alcohol.

The effect that branched isomers have on the separation of n-alkanes and 1-alcohols in a supercritical fluid extraction process was investigated, with n-decane and 1-decanol as the respective normal alkane and primary linear alcohol, and two additional C<sub>10</sub>-alcohol isomers.

High pressure phase equilibrium measurements indicated that all the components differ substantially in solubility in supercritical CO<sub>2</sub>, hence justifying pilot plant measurements. The binary phase diagrams showed that the largest difference in solubility occurred for n-decane and 1-decanol with 3,7-dimethyl-1-octanol and 2,6-dimethyl-2-octanol having solubility pressures lower than that of 1-decanol but higher than that of n-decane. A feed stream containing approximately equal amounts of 1-decanol, 3,7-dimethyl-1-octanol, 2,6-dimethyl-2-octanol and n-decane was separated with supercritical CO<sub>2</sub>.

A 28 mm diameter column equipped with a total of 4.32 m Sulzer DX packing and temperature and pressure operating limits of 150 °C and 300 bar respectively, was used in the pilot plant tests. During the pilot plant tests the operating temperature and pressure of the extraction column, were varied to determine the effect thereof on the overheads to feed ratio and selectivity. For the same operating temperature, it was found that a higher operating pressure leads to a higher overheads to feed ratio, as well as better selectivity for the light components. When comparing runs with pressure-temperature combinations that produce the same overheads to feed ratio, the higher operating temperature runs lead to product streams with a wider distribution of components. A low operating temperature thus increases the selectivity of the solvent. Interesting results were also found for runs operated with different solvent to feed ratios.

## INTRODUCTION

The alcohols of industrial importance include short chain alcohols ( $C_1 - C_5$ ), the plasticizer alcohols ( $C_6 - C_{11}$ ) and the fatty alcohols ( $C_{12} - C_{18}$ ) [1]. There are a number of different chemical processes that can be used to synthesize these alcohols. The alcohols, once manufactured, are used in many different applications. The specific application determines how pure the alcohol must be. Alcohols are commercially sold as either a very expensive pure product or a more popular and more often than not cheaper mixture of isomeric compounds and alcohols with different numbers of carbon atoms [1]. The use of these mixtures is advantageous in some applications, but in others, they can hinder the performance of the subsequent processes.

One of the production processes often used in the manufacturing of alcohols, is the oxidation of saturated hydrocarbons. Usually a mixture of n-alkanes with carbon numbers between 10 and 18 are brought into contact with an air-nitrogen mixture in the presence of a metaboric acid to form metaboric acid esters. The metaboric acid esters are then hydrolysed with water in a second step to form alcohols. To obtain economically acceptable selectivities, the conversion is kept below 20% [1]. Impurities are removed from the alcohol product and after fractional distillation, secondary alcohols with purities of greater than 98% are obtained [1]. The starting materials and the oxidation byproducts are usually removed with flash evaporation, cleaned in alkaline scrubbers, and the n-alkanes recycled. The large costs involved with the recovery of the n-alkanes and boric acid hindered the further development of this process. The alcohols generated in this process are usually converted to alkylphenols which are ethoxylated and used in nonionic surfactants and detergents.

During the ethoxylation process, ethylene oxide units are added to the alcohol to produce alcohol ethoxylates. If no post-production separation process was implemented in the alcohol manufacturing process, unreacted alkanes will still be present in the feedstock of the ethoxylation process. Current ethoxylation processes causes large amounts of residual alcohol to remain in the product stream [2]. Schwarz et al. [2] investigated the possibility of a post-production separation process that can be implemented to remove any residual alcohols, n-alkanes and lower alcohol ethoxylates from the higher alcohol ethoxylates. The process suggested and proven to be viable was a supercritical fluid extraction process with propane as the supercritical solvent. The process was considered as a possible separation process after high pressure phase equilibria measurements showed a significant difference in solubility of the alcohols and n-alkanes, compared to the alcohol ethoxylates, in supercritical propane. Even though the study by Schwarz et al. [2] focussed on high molecular mass alkanes and alcohols, the same trends are expected to occur for the low molecular mass alkanes and alcohols.

To make the alcohol ethoxylation process more economically viable, the unreacted alcohols and alkanes can possibly be recycled to the respective points in the manufacturing process where they are used as starting materials. To make this possible, the overheads product from the supercritical fluid extraction process proposed by Schwarz et al. [2] must be further processed to separate the alcohols from the n-alkanes. It has been proven that the solubility of alcohols differ from that of n-alkanes in supercritical fluids due to the presence of the functional end group in alcohols [3]. Supercritical fluid extraction thus came under consideration for a possible separation method. Bonthuys et al. [4] measured the high

pressure phase equilibrium data of 1-dodecanol and n-tetradecane in both supercritical CO<sub>2</sub> and ethane, and proved through a relative solubility analysis that it may be possible to separate the specific alcohol and n-alkane. These compounds were chosen due to the fact that they have boiling points closest to one another of all the alcohols and n-alkanes in the detergent range, i.e. with carbon numbers between 12 and 14. If a traditional separation technique like distillation were to be used to separate a mixture of alcohols and n-alkanes within this range, these two compounds would be the hardest to separate. If supercritical fluid extraction proves to be able to separate these two compounds with ease, it would be the preferred separation method.

Pilot plant tests confirmed that 1-dodecanol and n-tetradecane can be separated from one another. The influence of the process parameters on the performance of the separation technique was investigated in a follow-up study [5]. The performance of the supercritical fluid extraction process was gauged by the overheads to feed ratio and the selectivity. For the first part of the study [4] a feed mixture of 50% 1-dodecanol and 50% n-tetradecane was used and the overheads to feed ratio was maintained at 0.5 by manipulating the operating pressure. Other process parameters such as the operating temperature, solvent to feed ratio, reflux ratio and feed position, were then varied and the influence thereof on the selectivity was determined. It was found that low operating temperatures lead to better selectivity, while higher operating temperatures allows for better controllability. A lower solvent to feed ratio does not only lead to better separation, but also reduces the energy input requirement, as less solvent need to be heated and compressed to obtain supercritical conditions. The use of a reflux stream improves the process performance significantly when supercritical CO<sub>2</sub> is used as the solvent. With supercritical ethane as the solvent, the process performs extremely well, and reflux does not significantly improve the already good performance.

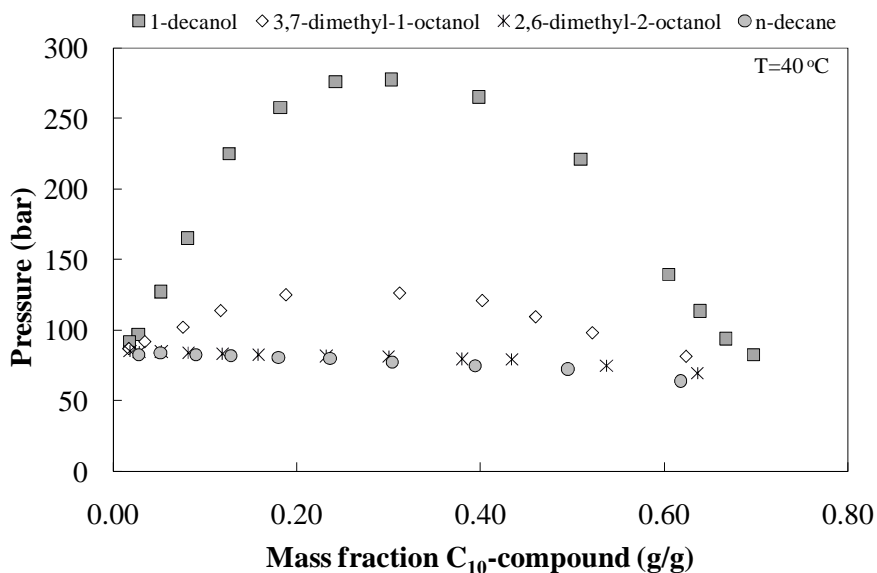
Most alcohol production processes lead to the formation of not only the primary linear alcohol, but also small amounts of structural isomers. The possibility thus exists that alcohol isomers might be present in the mixture of 1-alcohols and n-alkanes. Since it was assumed in previous studies that only the primary linear alcohol was present, it was decided to investigate if the presence of these isomers affect the separation of alcohols and n-alkanes, and if so, how the presence of the alcohol isomers affect the performance of the supercritical fluid extraction process.

## **HIGH PRESSURE PHASE EQUILIBRIUM MEASUREMENTS**

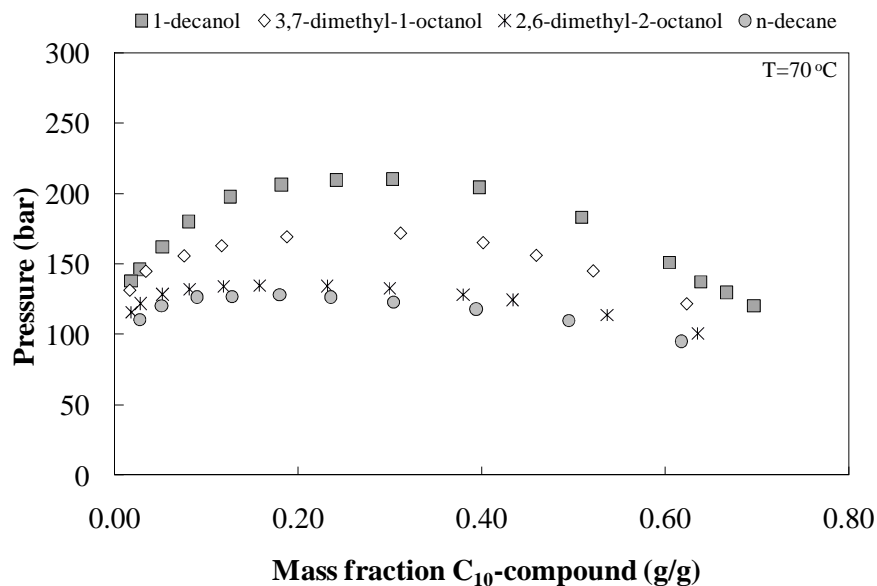
The literature provided measured high pressure phase equilibria data for binary mixtures of n-decane, 1-decanol and other C<sub>10</sub>-alcohol isomers in supercritical CO<sub>2</sub> [6]. A comparison of the phase equilibrium behaviour of binary mixtures of the C<sub>10</sub>-compounds and supercritical CO<sub>2</sub>, gave an indication of whether a supercritical fluid extraction separation process would be viable. If a significant difference in solubility exists for the respective compounds, the binary phase diagrams will also reveal the operating range of such a supercritical fluid extraction process.

Binary phase equilibrium measurements were done for supercritical CO<sub>2</sub> and each of the following C<sub>10</sub>-compounds: 1-decanol; 3,7-dimethyl-1-octanol; 2,6-dimethyl-2-octanol; and n-decane. The high pressure phase equilibria measurements were conducted in a high

pressure view cell at five temperatures between 35 °C and 75 °C. In Figures 1 and 2 the phase equilibria data of the four C<sub>10</sub>-compounds are presented at temperatures of 40 °C and 70 °C, respectively.



**Figure 1: Comparison of the solubility of 1-decanol; 3,7-dimethyl-1-octanol; 2,6-dimethyl-2-octanol and n-decane in supercritical CO<sub>2</sub> at 40 °C [6]**



**Figure 2: Comparison of the solubility of 1-decanol; 3,7-dimethyl-1-octanol; 2,6-dimethyl-2-octanol and n-decane in supercritical CO<sub>2</sub> at 70 °C [6]**

From the high pressure phase equilibria measurements it is clear that n-decane is the most soluble in supercritical CO<sub>2</sub> and 1-decanol is the least soluble in supercritical CO<sub>2</sub>. It would thus be possible to separate the primary linear alcohol from the corresponding alkane with the use of supercritical CO<sub>2</sub> in an extraction process. The two C<sub>10</sub>-alcohol isomers have solubilities ranging between that of 1-decanol and n-decane. The phase behaviour of 2,6-dimethyl-2-octanol is very close to that of n-decane, and it may prove difficult if not impossible to separate 2,6-dimethyl-2-octanol from n-decane. It should be noted that the binary phase diagrams have limited use when a multi-component mixture is used as a feedstock to the extraction column. Interactions among the C<sub>10</sub>-compounds may exist, which will affect the behaviour of the mixture with supercritical CO<sub>2</sub>. However, only long chain alkanes and alcohols, which are generally considered as non-interactive species, are present, and therefore it is assumed that the phase behaviour of the multi-component mixture will not be significantly different from the phase behaviour of the respective binary mixtures.

From the high pressure phase equilibria data the operating pressure of the extraction column can be estimated. The aim of the separation process will determine which compounds are to be separated from which. In this case two possibilities will be investigated. Firstly the aim may be to remove all the alkane from the alcohol mixture. This will mean that the extraction column will be operated at a pressure just above the mixture critical pressure of n-decane. This will allow most of the n-decane to solubilize in the supercritical CO<sub>2</sub> and report to the overheads product. Another possible aim may be to separate the primary linear alcohol from the multi-component mixture. This would mean that the extraction column be operated at a pressure just below the critical pressure of 1-decanol and above the critical pressures of all other components. Results should then indicate that most of the 1-decanol will be present in the bottoms product.

## PILOT PLANT EXPERIMENTS

A feed mixture comprising of approximately 25 mass% each of 1-decanol, 3,7-dimethyl-1-octanol, 2,6-dimethyl-2-octanol and n-decane were used. Experiments were conducted at two temperatures, 40 °C and 70 °C. Two solvent to feed ratios were investigated: a low solvent to feed ratio of approximately 20 and a high solvent to feed ratio of approximately 30. At the respective temperatures and concentrations of each component in the solvent, the two different operating pressures were selected from the high pressure phase equilibria diagrams (Figures 1 and 2).

The performance of the process was evaluated by considering two parameters: the overheads to feed ratio and the selectivity. The overheads to feed ratio is calculated by using the respective flow rates of the feed and overheads product and represents the mass fraction of the feed that reports to the overheads product. This value should ideally be close to the total mass fraction of the components required to be extracted from the feed mixture. For example, if it is required that only n-decane be removed from the feed mixture, an overheads to feed ratio close to 0.25 would indicate good performance.

$$\text{Overheads} / \text{Feed} = \frac{M_{\text{feed}}}{M_{\text{overheads}}} \quad (1)$$

The second parameter used to gauge the process performance is the selectivity (Equation 2). The selectivity is a measure of how well the solvent can select one component from the mixture and report it to the overheads product. The selectivity is the ratio of the mass fraction of a certain compound in the overheads product to the mass fraction of that compound in the bottoms product. If the selectivity is high it means that the solvent was able to dissolve the particular component very well from the feed mixture. A very low selectivity, on the other hand, indicates that the majority of that component was not extracted by the solvent, and consequently reported to the bottoms product. If the selectivity of a component is close to 1, it means that that component is distributed throughout both the overheads and bottoms product and effective separation was not achieved.

$$S = \frac{m_{overheads}}{m_{bottoms}} \quad (2)$$

### Experimental Set-up

A previously constructed pilot plant setup was used to do the experiments. A schematic representation of the pilot plant is given in Figure 3. A detailed description of the pilot plant can be found in Bonthuys et al. [4] and Crause [7].

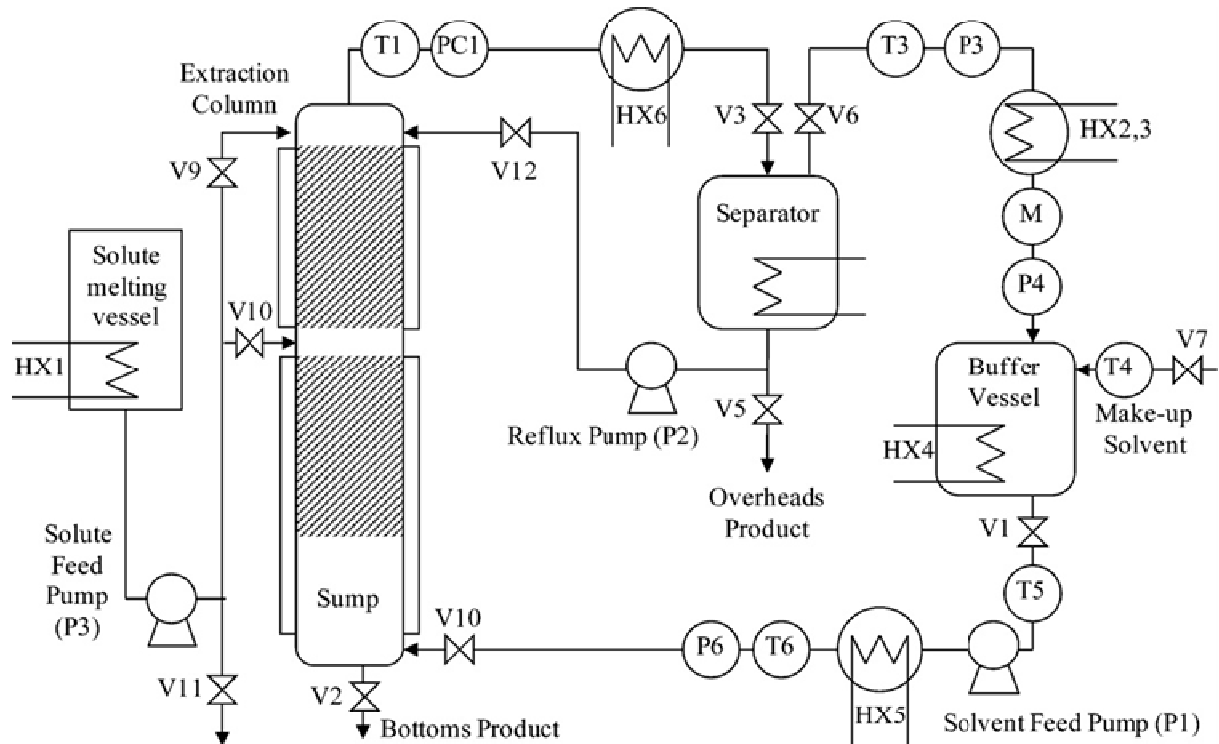


Figure 3: Schematic representation of the pilot plant set-up

The pilot plant consists of a 28 mm diameter column with two 2.16 m tall sections of Sulzer DX packing. The maximum operating pressure of the extraction column is 300 bar and the maximum operating temperature is 150 °C. The supercritical fluid extraction unit operates in the following manner: the supercritical solvent is fed from a buffer vessel where it is kept in a subcooled condition. The solvent moves from the buffer vessel to the solvent pump, where it is compressed to the operating pressure. The compressed solvent is then heated to the operating temperature with a heat exchanger to allow it to reach its supercritical state. It then enters the extraction column from the bottom and moves up through the packing until it reaches the top of the column. At the same time the solute feed mixture, in a heated liquid state, is fed from the top of the column and allowed to move downwards through the packing material. The solvent and solute pumps are adjusted to maintain a certain solvent to feed ratio throughout the duration of the experiment. The packing material enhances the contact between the solute feed mixture and the supercritical solvent. The supercritical solvent selectively extracts certain compounds from the feed mixture, depending on the operating conditions. The solvent loaded with the extracted components then moves from the top of the column to the separator vessel where the temperature is increased and the pressure is decreased to the solvent vapour pressure. The change in conditions reduces the solubility of the compounds in supercritical CO<sub>2</sub> and they precipitate as small droplets in the separator vessel. These components are removed from the separator vessel and present the overheads product. The rest of the feed components not extracted by the CO<sub>2</sub> collect at the bottom of the extraction column and are removed as the bottoms product. After the solutes have precipitated from the solvent in the separator vessel, the solvent flows through a cooler where it is condensed, and finally reaches the buffer vessel again. The solvent is then recycled back to the column.

The accuracies of the measured values of temperature, pressure and flow rate, are as follows:

- Temperature sensors T1 and T6 have an accuracy of 0.4 °C while T3, T4 and T5 are measured to an accuracy of 0.5 °C.
- Pressure gauge P1 is accurate to 1.5 bar while P3, P4 and P6 are accurate to 2 bar.
- The solute feed flow rate, as well as the overheads and the bottoms flow rates are measured to an accuracy of 1 % while the solvent flow rate is measured with an accuracy of 3 %.
- Gas chromatographic analyses were performed on a Varian 3400 gas chromatograph equipped with a 60 m long Phenomenex Zebron ZB-5 column with an inside diameter of 0.32 mm, 0.25 µm packing and a FID detector. Results from duplicate diluted samples show an error margin of less than 1.5 %.

## **Results and Discussion**

Runs 1, 2 and 3 were conducted at an operating temperature of approximately 40 °C and Runs 4, 5 and 6 were conducted at an operating temperature of approximately 70 °C. The solvent to feed ratio was varied for Runs 3 and 6. At the respective operating temperatures and the selected solvent to feed ratios, the operating pressures were determined from Figures 1 and 2. The results of the pilot plant runs at different operating conditions are presented in Table 1.

**Table 1: Summary of pilot plant experiments and results**

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
<b>Solvent</b>	<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>	<b>CO<sub>2</sub></b>
<b>T1 (°C)</b>	<b>42.7</b>	<b>43.5</b>	<b>42.2</b>	<b>71.3</b>	<b>70.9</b>	<b>71.3</b>
T3 (°C)	55.7	53.7	56.1	70.0	71.3	72.2
T4 (°C)	14.2	14.1	10.5	13.7	12.3	13.7
T5 (°C)	3.9	3.0	3.4	3.6	2.5	3.2
T6 (°C)	39.9	41.2	39.2	70.5	70.0	70.7
<b>P1 (bar)</b>	<b>90.0</b>	<b>93.0</b>	<b>90.0</b>	<b>130.0</b>	<b>136.0</b>	<b>131.0</b>
P3 (bar)	50.0	50.0	46.0	50.0	50.0	51.0
P4 (bar)	49.0	49.0	45.0	49.0	48.0	50.0
P6 (bar)	89.0	92.0	89.0	128.0	132.0	128.0
Solvent flow rate (kg/h)	15.2	14.9	14.3	15.0	14.4	14.6
Feed flow rate (kg/h)	0.839	0.839	0.482	0.808	0.772	0.499
<b>Solvent/Feed Ratio</b>	<b>18.1</b>	<b>17.8</b>	<b>29.7</b>	<b>18.6</b>	<b>18.7</b>	<b>29.3</b>
Overheads flow rate (kg/h)	0.434	0.565	0.319	0.435	0.536	0.356
Bottoms flow rate (kg/h)	0.404	0.274	0.163	0.372	0.236	0.142
<b>Overheads / Feed Ratio</b>	<b>0.52</b>	<b>0.67</b>	<b>0.66</b>	<b>0.54</b>	<b>0.69</b>	<b>0.71</b>
% 1-decanol in feed	27.1	27.1	26.9	28.5	26.1	27.2
% 1-decanol in overheads	14.6	16.0	14.5	16.6	15.2	17.2
% 1-decanol in bottoms	43.3	51.7	52.7	44.6	51.5	56.0
% n-decane in feed	28.5	28.0	26.4	26.9	27.8	27.7
% n-decane in overheads	47.4	39.7	37.6	42.0	38.8	34.8
% n-decane in bottoms	4.6	3.0	3.5	7.0	5.3	5.8
% 3,7-dimethyl-1-octanol in feed	23.4	23.6	23.7	23.2	22.9	22.9
% 3,7-dimethyl-1-octanol in overheads	15.5	17.3	30.7	16.8	17.4	19.2
% 3,7-dimethyl-1-octanol in bottoms	33.1	31.2	40.0	31.2	38.4	32.7
% 2,6-dimethyl-2-octanol in feed	21.0	21.3	23.0	21.3	23.2	22.3
% 2,6-dimethyl-2-octanol in overheads	22.5	27.0	17.2	24.7	28.6	28.8
% 2,6-dimethyl-2-octanol in bottoms	19.0	8.1	3.8	17.2	4.8	5.6
<b>Selectivity for</b>						
<b>1-decanol</b>	<b>0.34</b>	<b>0.31</b>	<b>0.27</b>	<b>0.37</b>	<b>0.30</b>	<b>0.31</b>
<b>n-decane</b>	<b>10.29</b>	<b>13.38</b>	<b>10.83</b>	<b>6.00</b>	<b>7.36</b>	<b>6.01</b>
<b>3,7-dimethyl-1-octanol</b>	<b>0.47</b>	<b>0.47</b>	<b>0.43</b>	<b>0.54</b>	<b>0.45</b>	<b>0.59</b>
<b>2,6-dimethyl-2-octanol</b>	<b>1.18</b>	<b>3.34</b>	<b>8.07</b>	<b>1.44</b>	<b>5.98</b>	<b>5.17</b>

The results indicate that supercritical CO<sub>2</sub> is able to distinguish between n-decane, 1-decanol and the two C<sub>10</sub>-alcohol isomers.

When operating at a higher pressure, at the same operating temperature, the overheads to feed ratio increases. This is to be expected, since the solvent power of supercritical CO<sub>2</sub> increases



at higher pressures. The selectivities of the light components also increased at higher operating pressures. This means that at higher operating pressures the solvent is able to distinguish better between the components, and thus selectively extracts the light components from the feed mixture. However, because a multi-component mixture is used, a higher selectivity of n-decane does not necessarily mean a purer overheads product. As the selectivity for n-decane increases, so does the selectivity of 2,6-dimethyl-2-octanol. None of the experimental conditions used in this investigation were able to produce product streams of very high purity. In order to achieve a high purity n-alkane or 1-alcohol product, additional extraction columns will have to be added to the setup to process the product streams further.

For all the runs the bottoms product consisted of approximately 40-50% 1-decanol and the overheads product consisted of approximately 30-40% n-decane. These results indicate that the supercritical fluid extraction process with CO<sub>2</sub> as the solvent is able to produce two product streams, each concentrated in either the heavy or the light component. The isomers distribute themselves among the two product streams, with 3,7-dimethyl-1-octanol behaving more like 1-decanol, and 2,6-dimethyl-2-octanol behaving more like n-decane. These behavioural trends were also evident in the binary phase equilibria data presented in Figures 1 and 2.

The runs that were conducted at a higher solvent to feed ratio had an increased overheads to feed ratio. This means that a larger fraction of the feed mixture reported to the overheads product. The question now arises whether the increase in the overheads to feed ratio is due to more light or more heavy components reporting to the overheads product. From the results in Table 1 it is clear that the selectivity of the lightest component, i.e. n-decane, stays the same for Runs 1 and 3, and Runs 4 and 6. The main difference between the selectivities of Runs 1 and 3, and Runs 4 and 6, can be seen for the second lightest component, 2,6-dimethyl-2-octanol. The selectivity of 2,6-dimethyl-2-octanol drastically increases with an increase in the solvent to feed ratio. The selectivities of the heavier components, the 1-decanol and 3,7-dimethyl-1-octanol, seem to slightly decrease with an increase in solvent to feed ratio.

As the solvent to feed ratio increases, more solvent is available per amount of feed mixture. At the selected operating conditions the solvent thus preferentially dissolves the lightest component, but because more solvent is now available more of the other light components (especially the second lightest component) can thus also be dissolved, before the solvent reaches its capacity.

If the aim is to have an as pure as possible overheads product, with a majority of n-decane present, a lower solvent to feed ratio is thus preferred.

## CONCLUSIONS

The results presented in this paper show that it is possible to utilize CO<sub>2</sub> as a solvent in a supercritical fluid extraction process to separate a feed stream of approximately equal amounts of n-decane, 1-decanol, 3,7-dimethyl-1-octanol and 2,6-dimethyl-2-octanol. The operating conditions of the supercritical fluid extraction process can be manipulated to

produce two product streams, each one concentrated in either the heavy, or the light component.

The binary phase diagrams of the each of the components present in the feed stream with supercritical CO<sub>2</sub> aided in the selection of possible temperature-pressure combinations to test on the supercritical pilot plant. For the same operating temperature, a higher operating pressure leads to an increased selectivity, and consequently more pure overheads and bottoms products. Results of runs that produced the same overheads to feed ratio, show that a higher operating temperature leads to a decrease in the selectivity of the solvent.

To produce two product streams of high purity, the operating conditions must be selected to allow operation at the lowest possible operating temperature, accompanied by the highest possible operating pressure. A low solvent to feed ratio is beneficial with regard to the energy requirements of the process, and also lead to acceptable separation performance. The limits of the operating pressure and temperature are governed by the phase behaviour of the components in the systems, and can to a certain extent be deduced from the binary phase diagrams.

Future work includes the investigation of the influence of other operating parameters e.g. reflux ratio and feed position, on the overheads to feed ratio and selectivity. Once a wide variety of operating conditions have been studied experimental results can be compared to that produced by popular process simulators.

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