

# SEPARATION OF ALKANES AND ALCOHOLS WITH SUPERCRITICAL FLUIDS

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## 1 INTRODUCTION

Saturated alcohols with between 8 and 20 hydrocarbon atoms, particularly 12 to 14 carbon atoms, are often used in the production of detergents, either directly as an alcohol or after ethoxylation as an alcohol ethoxylate [1]-[3]. These alcohols are often produced by oxygenating alkanes, or rather a mixture of alkanes, with air or oxygen in the presence of a catalyst such as boric acid [4]. However, on industrial scale the oxygenation of the alkane to the alcohol is often incomplete. Application of these alcohols often requires low residual alkane content and a post production separation process is thus required.

Typically the oxygenation process results in a product stream with a distribution of both alkanes and alcohols around the mean hydrocarbon backbone. The post production separation technique employed should be able to distinguish between the alkane and the alcohol and not be very molecular weight dependent. Crossover melting and boiling points prevent the successful implementation of traditional processes such as distillation and crystallisation.

It has previously been shown that the phase equilibria of waxy and detergent range alcohols in supercritical propane differ from that of the corresponding alkane in supercritical propane [5], [6] indicating that it may be possible to separate detergent range alcohols from their corresponding alkanes using supercritical fluids.

To model the alkane – alcohol mixture a feed with an average of 13 carbon atoms was selected with a large number of the molecules having between 12 and 14 carbon atoms. This molecular weight range is very common for use in detergent range products [1]-[3]. To simplify the problem only alkanes and alcohol with between 12 and 14 carbon atoms were considered.

Generally the presence of the hydroxyl group as well as an increase in the number of carbon atoms decreases the solubility [7]-[9] in supercritical solvents. For the alkane/alcohol mixture under consideration, the most difficult separation is thus that of the alcohol with the least number of carbon atoms, i.e. dodecanol (alcohol with 12 carbon atoms) and the alkane with the most number of carbon atoms, i.e. tetradecane (alkane with 14 carbon atoms). To model the system, it was assumed that the hydrocarbon backbone is linear and the alcohol is primary. 1-Dodecanol and n-tetradecane were used. If it is possible to separate these two compounds, it should be possible to separate an industrial mixture.

Based on their suitable critical properties, ethane and carbon dioxide were selected as supercritical solvents to be investigated. An operating temperature range of between 310 and 355 K was selected in order to minimise thermal decomposition and utilise the properties of supercritical fluids to their best.

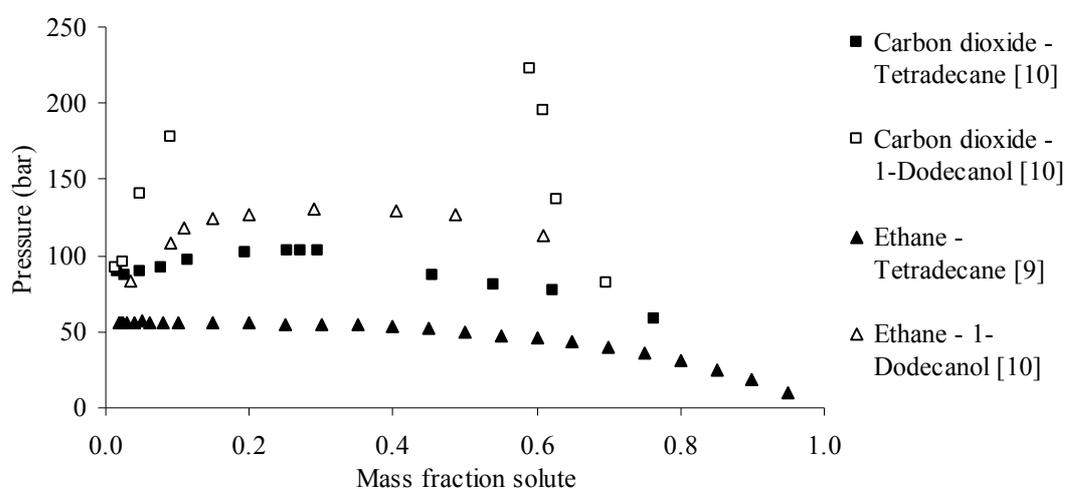
The aim of this work is to determine the technical viability of using supercritical carbon dioxide or ethane to separate detergent type alcohols from their corresponding alkanes by considering a mixture of tetradecane and 1-dodecanol. The work constitutes two parts: Firstly a comparison of the high pressure solubility of tetradecane and 1-dodecanol in ethane and in carbon dioxide and secondly pilot plant testing of the ability of supercritical ethane to separate a 50 % - 50 % mixture of tetradecane and 1-dodecanol.

## 2 HIGH PRESSURE SOLUBILITY MEASUREMENTS

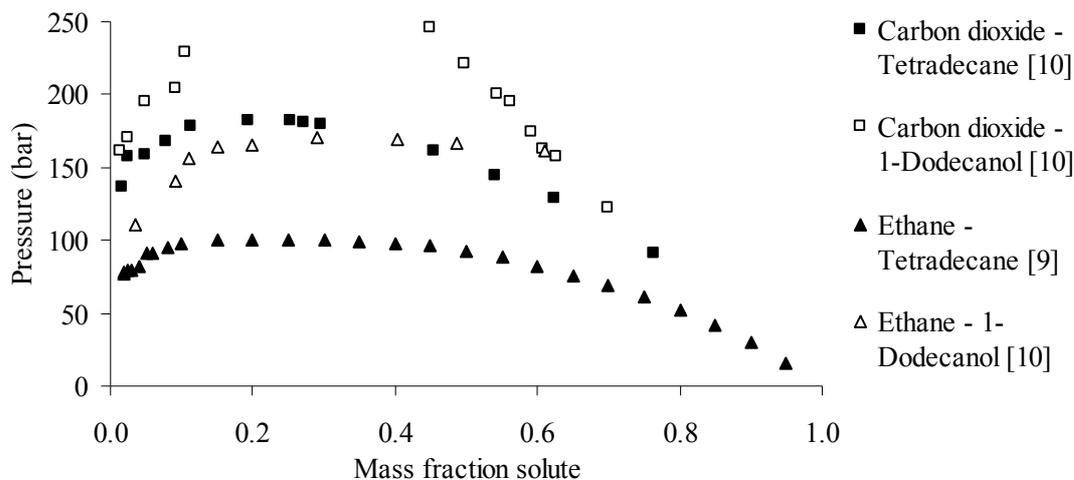
Prior to expensive and time consuming pilot plant tests, the solubility of 1-dodecanol and tetradecane in supercritical ethane and carbon dioxide had to be compared. This gave an indication of the selectivity of the solvents and provided insight into possible operating pressures. Bonthuys measured solubility data for the systems carbon dioxide – tetradecane, carbon dioxide – 1-dodecanol and ethane – 1-dodecanol [10] while ethane – tetradecane data was obtained from Schwarz et al. [9]. Figure 1 and Figure 2 show comparisons of the solubility of tetradecane and 1-dodecanol in ethane and carbon dioxide at 313 and 353 K respectively.

It can be seen that for both ethane and carbon dioxide a difference in phase equilibria exists, indicating that both supercritical ethane and carbon dioxide should be able to fractionate the model mixture. The presence of the hydroxyl group has a significant effect on the solubility resulting in a lower solubility and thus higher pressures for 1-dodecanol compared to tetradecane. As a decrease in solubility occurs with an increase in hydrocarbon backbone length [7][8][11], two molecules with the same hydrocarbon backbone will have an even larger difference in solubility.

The difference in the phase equilibria is larger for carbon dioxide than for ethane, yet the pressures for ethane are lower than those for carbon dioxide. When comparing the solubility at the two temperatures, it is evident that the solubility difference for both solvents is larger at 313 K than at 353 K and thus it is expected that the selectivity will be higher at lower temperatures.



**Figure 1: Comparison of the solubility of tetradecane and 1-dodecanol in supercritical carbon dioxide and ethane at 313 K**



**Figure 2: Comparison of the solubility of tetradecane and 1-dodecanol in supercritical carbon dioxide and ethane at 353 K**

The phase equilibria results indicate that both solvents may be able to separate tetradecane and 1-dodecanol. However, the phase equilibria data is not sufficient to choose between the two solvents. Pilot plant tests were thus conducted for both solvents. To investigate the difference in temperature, pilot plant testing were conducted at 313 and 353 K.

### 3 PILOT PLANT EXPERIMENTS

The aim of the pilot plant testing is to determine if supercritical ethane and / or carbon dioxide is able to separate tetradecane and 1-dodecanol and the extent to which it is possible. A 50 – 50 mass percent feed was considered. The operating pressures were selected so that approximately half the feed is removed in the overheads (determined experimentally).

#### 3.1 Experimental Methods

A schematic representation of the pilot plant set-up used is given in Figure 3. A detailed description of the pilot plant and testing thereof against reliable literature data is given by Crause et al [12].

The core of the pilot plant is a heated and insulated, 5 m tall, 29 mm inner diameter column, equipped with two 2.16 m sections of Sulzer DX packing and a sump at the bottom. The pilot plant has a maximum operating pressure and temperature of 300 bar and 420 K respectively. Heated solute is introduced in the middle of the column and the supercritical solvent is introduced at the bottom of the column. The loaded solvent exits at the top of the column after which it expands over a pressure control valve into a heated separator, where the solvent and solute are allowed to separate. The separator is operated at the solvent storage pressure. The solvent exits the separator and is condensed through a heat exchange before returning to the solvent buffer vessel, from where it is recycled. The overheads and bottoms products are removed periodically from the separator and sump respectively.



although the difference in the carbon dioxide solubility pressures is larger, at the operating conditions (pressure and temperature) there is not such a large difference in the solubility of tetradecane and 1-dodecanol in carbon dioxide.

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

	Run 1	Run 2	Run 3	Run 4
Solvent	CO <sub>2</sub>	CO <sub>2</sub>	Ethane	Ethane
T1 (°C)	41.1	81.3	41.2	70.5
T3 (°C)	35.5	71.5	36.6	61.1
T4 (°C)	18.2	18.3	19.5	18.2
T5 (°C)	8.6	8.5	8.5	8.7
T6 (°C)	41.1	81.3	41.2	70.5
P1 (bar)	95.5	149.1	60.9	89.3
P3 (bar)	62	61	50	41
P4 (bar)	50	50	42	38
P6 (bar)	92	145	57	85
Solvent flow rate (kg/s)	17	13	10.6	9.5
Feed flow rate (kg/s)	0.60	0.46	0.59	0.56
Overheads flow rate (kg/s)	0.35	0.24	0.37	0.31
Bottoms flow rate (kg/s)	0.25	0.22	0.22	0.25
Overheads / Feed Ratio	0.58	0.52	0.63	0.56
% Tetradecane in feed	50	50	50	50
% Tetradecane in overheads	64	65	79	79
% Tetradecane in bottoms	29	36	1	20
% 1-Dodecanol in feed	50	50	50	50
% 1-Dodecanol in overheads	36	35	21	21
% 1-Dodecanol in bottoms	71	64	99	80
Selectivity	2.2	1.8	79	4.0

In addition to investigating the effect of the different solvents, the pilot plant experiments also investigated the effect of temperature. For both solvents, an increase in temperature lead to a lower selectivity. This can be explained by considering Figure 1 and Figure 2: At the lower temperature the solubility difference is higher, resulting in a higher selectivity.

#### 4 CONCLUSIONS AND FUTURE WORK

This work has proven that it is technically viable to use both supercritical carbon dioxide and supercritical ethane to separate detergent type alcohols from their corresponding alkanes. This was achieved by considering a model feed of 50 % tetradecane and 50 % 1-dodecanol.

The phase equilibria data was compared and it was found that a significant difference in solubility of tetradecane and 1-dodecanol exists for both solvents. Pilot plant tests showed that both carbon dioxide and ethane are able to fractionate the model feed indicating that it is technically viable to separate detergent range alcohols from their corresponding alkanes.

It was found that the selectivity is higher at lower temperatures. Ethane showed a higher selectivity and lower operating pressure and thus seems the better of the two solvents.

However, it should be remembered that ethane is flammable and considerably more expensive than carbon dioxide. In addition, as only four experimental runs were conducted, insufficient information is available as yet to make a sensible choice between the two solvents. Further investigations in this regards are required.

This paper contains work pertaining to a preliminary technical feasibility study and a large amount of future work still needs to be conducted. Pilot plant testing was conducted at a single pressure, solvent flow rate and feed composition with the feed in the middle of the column and with no reflux. These parameters need to be varied to determine the optimum operating conditions for a set feed composition.

The system investigated here was modelled as consisting of tetradecane and 1-dodecanol. Typical industrial mixtures consist of a range of alkanes and alcohols and may also contain a significant amount of branched molecules. The bulk may thus behave different to the molecules used in this work. The influence of a range of molecular weight as well as side branches in molecules thus needs to be investigated.

In addition to technical feasibility, an economic analysis needs to be conducted to determine the economic viability of such a process.

## 5 ACKNOWLEDGEMENTS

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