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Separation of alkanes and alcohols with supercritical fluids. Part I: Phase equilibria and viability study

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ABSTRACT

The chemical conversion of detergent range alkanes (12–14 carbon atoms) to alcohols is often incomplete and results in a large amount of residual alkane. This paper shows that these alkanes and alcohols can be separated by supercritical fluids. Ethane, propane and carbon dioxide were selected as possible supercritical solvents while n-tetradecane and 1-dodecanol were selected to represent the alkane–alcohol mixture, as these would be the two most difficult compounds to separate in a C12 to C14 alkane–alcohol mixture. A phase behaviour study and relative solubility analysis revealed that both ethane and carbon dioxide show promise in separating n-tetradecane and 1-dodecanol. Propane was eliminated as possible solvent because the phase behaviour of n-tetradecane and 1-dodecanol in supercritical propane is too similar. A pilot plant study showed that both supercritical ethane and carbon dioxide can be used to separate n-tetradecane and 1-dodecanol, with indications that supercritical ethane may affect a superior separation. An economic analysis, considering the energy requirements, revealed that the most important parameter with regard to energy consumption is the solvent-to-feed ratio. The process utilising ethane is more energy intensive, yet the energy requirements for both processes compare well with other petrochemical separation processes using supercritical fluids. Further investigations with both ethane and carbon dioxide should be conducted to determine which of these two solvents are superior and to optimise the operating parameters.

1. Introduction

Developments in the field of liquid detergents and cosmetics have increased the demand for surfactants, processing aids and emollients. Alcohols are often used in these products where they serve as solvents, adjust the viscosity and act as surfactants. Industrial scale oxygenation of the alkane to the alcohol is often incomplete, resulting in a significant amount of residual alkane. Application of these alcohols often requires a low residual alkane content, necessitating a post-production separation process. Traditional separation methods such as distillation and crystallisation are not technically viable, as crossover boiling [1,2] and melting [3] points prevent the successful implementation of such processes. Values of selected boiling and melting points for alkanes and alcohols with between 10 and 16 carbon atoms are summarised in Table 1, illustrating possible problems associated with separation processes based on boiling and melting point differences.

Previous studies on the processing of petrochemicals with supercritical fluids have shown that supercritical fluids are attractive alternatives to traditional solvents. They are able to separate molecules with different hydrocarbon backbone lengths [4–7]. Furthermore, they are able to distinguish between molecules with different functional groups [8] and even between molecules with similar functional groups at different positions on the hydrocarbon backbone [9]. This is possible while affording lower operating temperatures than traditional processes, thus preventing thermal decomposition.

The aim of this paper is to show that supercritical fluid extraction is a viable method to separate a mixture of detergent range alkanes and alcohols and that the energy requirements are comparable to other supercritical fluid separation processes. The alcohols being considered typically consist of an average of 13 hydrocarbon atoms with the majority of the molecules containing between 12 and 14 carbon atoms. High-pressure phase equilibria measurements show that, generally, an increase in the number of carbon atoms as well as the presence of the hydroxyl group will increase the phase transition pressure and thus decrease the solubility of the molecules in supercritical solvents [6,7]. Supercritical fluids may thus be able to distinguish between these compounds. Assuming linear molecules with the hydroxyl group in the primary position and ignoring lower and higher homologous products, it is expected that the most difficult separation will be that of n-tetradecane (C14 alkane, nC14) and 1-dodecanol (C12 alcohol, 1-C12-OH) and the separation of these two compounds will thus be considered.

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Nomenclature

nC14	n-tetradecane
RSP	relative solubility product
SR	solubility ratio
x	mass fraction
1-C12-OH	1-dodecanol

Subscripts

B	refers to the bottoms product
L	refers to liquid phase
nC14	refers to n-tetradecane
O	refers to the overheads product
V	refers to vapour phase
1-C12-OH	refers to 1-dodecanol

Carbon dioxide, ethane and propane will be considered as possible supercritical solvents. Carbon dioxide is the most common supercritical solvent and has a suitable critical temperature of 304.2 K [1], hence its inclusion. However, carbon dioxide is not such a good solvent of high molecular mass petrochemical compounds as relatively high pressures are required for total solubility, resulting in high process pressures. Low molecular weight alkanes have recently been considered as attractive alternatives for carbon dioxide as supercritical solvents. In particular, ethane and propane show promise due to their suitable critical temperatures (305.3 and 369.8 K, respectively [1]) and the fact that they show improved solubility compared to carbon dioxide.

In order to show that supercritical fluids are able to separate nC14 and 1-C12-OH, this paper considers the following:

- Firstly, the phase behaviour of nC14 and 1-C12-OH in supercritical carbon dioxide, propane and ethane is considered. Previously published phase equilibria data were used for the analysis presented in this work. The phase behaviour is evaluated by comparing the phase behaviour of the alkane and the alcohol in the aforementioned supercritical solvents. Solvents that show a promising difference in phase behaviour between the alkane and the alcohol are subjected to a relative solubility ratio analysis. The aim of the relative solubility analysis is to determine if separation can be achieved and, together with the phase equilibria measurements, provide an indication of the possible operating conditions.
- Secondly, pilot plant tests are conducted to determine the technical viability of the process. Such experiments are limited to selected conditions to prove that the separation can be achieved, to obtain an indication of the degree of separation that can be achieved, and to provide sufficient information for an initial conceptual design.
- Lastly, the energy requirements for a typical separation process are estimated using a conceptual design based on the pilot plant results.

Table 1
Melting and boiling points of selected C10 to C16 alkanes and alcohols.

Compound	Normal boiling point (K) [1,2]	Melting point (K) [3]
n-Decane	447	243
n-Dodecane	489	264
n-Tetradecane	526	279
n-Hexadecane	560	291
1-Decanol	504	280
1-Dodecanol	532	297
1-Tetradecanol	562	313
1-Hexadecanol	607	322

2. Experimental methods

A previously constructed pilot plant set-up was used for the experimental measurements. A schematic representation of the pilot plant is shown in Fig. 1. The core of the pilot plant is a 28 mm diameter column equipped with a 4.32 m total packed height of Sulzer DX packing, capable of operating at a maximum operating temperature and pressure of 150 °C and 30 MPa, respectively.

The pilot plant operates as follows: the supercritical solvent enters the column at the bottom and moves up the column. The nC14/1-C12-OH mixture enters the column either in the middle or at the top of the column. The loaded solvent (with mainly nC14) then exits the column at the top while the residue (with mainly 1-C12-OH) exits the column at the bottom. The loaded solvent undergoes a pressure reduction, after which separation of the solvent and the extract occurs in the separation vessel. The solvent then enters the solvent recycle system where it is cooled, condensed and stored in the buffer vessel. From the buffer vessel the solvent is then sub-cooled, pumped to the operating pressure and then heated to the operating temperature. The pressurised, heated solvent is now ready to re-enter the extraction column.

The experimental set-up is controlled as follows: both the solvent and the solute flow rates are controlled by controlling the stroke length of the diaphragm metering pumps used to pump these fluids. The solute flow rate at a set stroke length is generally independent of pressure and the solute pump can thus be calibrated by obtaining a relationship between the stroke length and the solute flow rate. On the other hand, because the solvent is compressible, the solvent flow rate at a set stroke length is dependent on the operating pressure. Therefore, previous experience is used to obtain an initial estimate of the required stroke length of the solvent pump, after which the stroke length is adjusted to obtain the correct flow rate at the desired pressure. The solvent cycle is thus started before the solute is fed to the column to ensure the correct solvent flow rate. The pressure in the column is controlled by manipulating the release rate of the solvent from the column. Pressure controller (PC1 in Fig. 1) controls the degree to which valve V3 is opened, and thereby controls the pressure in the column. The temperature in the system is controlled by using two heating baths and a chilling unit. The heating baths control the temperature of hot water that is circulated around the column, separator, solvent pre-heater and solute melting vessels and, as heat tracing, along selected process lines. Previous experimental data, together with a trial and error method, is used to set the correct temperature. The chilling unit produces chilled water, which is used in the solvent recycle system to ensure that the solvent is fully condensed before it enters the storage vessel. The chilled water is also used to sub-cool the solvent before it enters the solvent pump.

Further details regarding the setup and experimental procedure are provided elsewhere [4,10,11]. For this specific project, the experiments were conducted within the following experimental boundaries:

- The temperature ranged between 40 °C and 70 °C (ethane) and 80 °C (carbon dioxide).
- The solvent flow rate was kept between 14 and 18 kg/h (equivalent to between 6.3 and 8.2 kg/(m^2 s)) for carbon dioxide and between 9 and 11 kg/h (equivalent to between 4.1 and 5.0 kg/(m^2 s)) for ethane. These values are in accordance with a previous study [4].
- In accordance with other supercritical fluid separation processes for high molecular mass petrochemicals, a solvent to feed ratio between 18 and 70 was selected for these tests [4,5,12]. The solute flow rate was varied to obtain the said solvent to feed ratios.