

CHAPTER 2

EXISTING METHODS FOR OXYGENATE REMOVAL

2.1 Introduction

A review of existing research serves to indicate the types and successes of separation processes considered and the approach used in each case.

Two processes for the removal of oxygenates are briefly discussed below:

2.2 Extractive distillation using water

Carlson, Smith & Morrell (1954:350) studied complex mixtures produced by hydrocarbon synthesis which contained light ($C_1 - C_5$ mostly) alcohols, aldehydes, ketones, esters and organic acids. Needless to say, the separation of these materials is very difficult. Most form binary azeotropes with other materials present in the mixture, especially water. To accomplish the isolation of the maximum number of pure compounds with a minimum number of steps, the authors reviewed many potential separation processes. Chemical methods considered include the following:

- i) aldolization of aldehydes,
- ii) acetalization of aldehydes,
- iii) hydrogenation of aldehydes and ketones to alcohols,
- iv) saponification of esters,
- v) oxidation of aldehydes to acids,
- vi) neutralization of acids,
- vii) complex formation of aldehydes and methyl ketones with sodium bisulfate.

Physical separation processes such as:

- i) superfractionation,
- ii) azeotropic distillation with selected entrainers,
- iii) azeotropic distillation at different pressure levels to shift azeotrope composition,
- iv) liquid-liquid extraction with a wide variety of solvents,
- v) extractive distillation with solvents of various degrees of polarity.

were also tested. Of the methods listed above, extractive distillation was found to be most satisfactory.

Despite violating conventional specifications for solvents, (as discussed in later chapters²), water was found to be a most effective solvent. It forms azeotropes with many of the products and reacts chemically with some, as in the hydrolysis of esters and acetals.

It was found that different classes of oxygenates could be separated due to the effect of a high water concentration on the relative volatilities of the groups involved.

2.3 Liquid-liquid extraction using a polar solvent

2.3.1 General

Quann and Tabak (1987) patented a process for removing oxygenated impurities from a hydrocarbon stream. A polar organic solvent mixture such as propylene carbonate and 2-aminoethanol is contacted with the hydrocarbon stream in a liquid-liquid extraction operation. The solvents are heavy boiling relative to the oxygenated compounds contained in and removed from the hydrocarbon stream. Recovery of the solvent can thus easily be

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- i) It should be high boiling relative to the materials to be separated.
 - ii) It should not form azeotropes with the products.
 - iii) It should not react with the products.

accomplished using ordinary distillation. The purified hydrocarbon stream is washed with water to improve solvent recovery. The solvent phase from the extractor and the water phase from the scrubber are combined to recover the solvent. The process is claimed to be effective for the removal of impurities such as alcohol, aldehyde, ketone or acid from a hydrocarbon stream comprising C₄-C₉ olefins.

2.3.2 Process Description

Refer to figure 2.1. The hydrocarbon feed is introduced to the bottom inlet of a continuous liquid-liquid extraction unit 4 wherein the feedstock is contacted in counterflow operation with the solvent. The solvent introduced is a combined stream composed of makeup solvent and a recycle stream.

The solvent extract phase, rich in oxygenates, is directed to distillation in solvent splitter 12. The extracted stream leaves the top of extractor 4 and is directed to water scrubber 18 for removal of solvent which has been carried from the liquid extractor. The purified olefin leaves via line 28 and is now ready for further processing. The solvent-containing water effluent from scrubber 18 is combined with the solvent extract phase from liquid extractor 4 prior to entering solvent splitter via line 14.

2.3.3 Solvent properties

The principle used in this process is the fact that oxygenates are far more soluble in a heavy organic polar solvent than olefins (1987:Abstract):

"Preferred solvents are oxygen containing organic solvents which are immiscible with hydrocarbons but not the oxygenates contained therein and are relatively high boiling relative to the oxygenates and hydrocarbons to be purified."

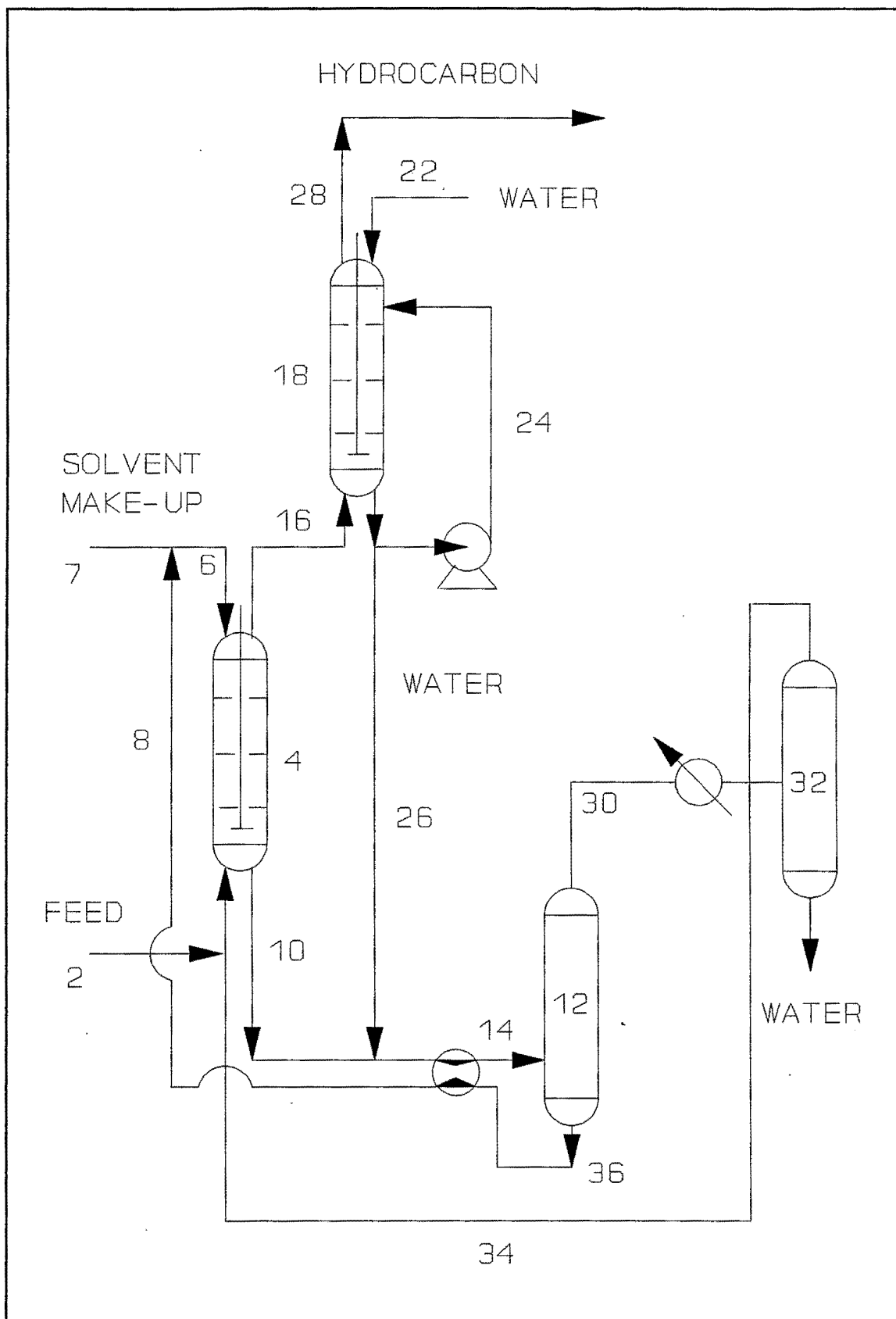


Figure 2.1: Patented extraction process.

"Polarity of the solvent may be expressed by reference to its

dielectric constant and dipole moment. Preferred organic solvents have a dielectric constant greater than 20, say about 30 to 50; and a dipole moment greater than about 0.6 Debye units."

"Organic solvents having these properties include compounds having carbonyl, hydroxyl, amino, ether, nitro, halogen groups, etc., such as propylene carbonate, monoethanolamine, furfural, dimethylsulfoxide and alkylene glycols. Most preferred solvents include propylene carbonate, monomethanol amine, furfural or any combination of these solvents." (p.1)

2.4 Summary

It should be considered that higher olefins are usually produced by oligomerisation of lighter olefins such as ethylene. In these light feed streams oxygenates can be relatively easily removed by a liquid-liquid phase water wash at low temperatures. The heavier product streams obtained from such processes differ from the SLO in terms of the types of contaminants present. Different reaction steps are involved, and as a result the SLO contains significant amounts of higher oxygenates not found in most other higher olefin streams. Consequently little work has been done on the removal of higher oxygenates.

Since the solubility of C8 SLO oxygenates (and thus also 2-hexanone) in water is insignificant, a water wash can probably not be used for a 2-hexanone / 1-octene separation (This option will be explored further in the next chapters). This leaves the extraction process as the only feasible one known.

Since the extraction process already exists, one may be prompted to ask: Why consider azeotropic or extractive distillation at all?

Gerster (1969:45) considered the technical feasibility and cost advantages of liquid-liquid extraction versus azeotropic or extractive distillation. While both permit separation between

classes of compounds, such as alcohols and an associated family of hydrocarbons, one negative aspect of extractors is that they can not be designed with as much confidence as in the distillation case, because throughputs, efficiencies and hydraulic operabilities are sensitive to the liquid properties and settling rates of the phases.

Sounders (see Gerster, 1969:45) computed the relative volatilities (α) in distillation, extractive distillation, and liquid-liquid extraction which are required to give equal plant cost. He assumed a 67% solvent concentration, and four times as much liquid to be handled in extractive distillation and in extraction as in ordinary distillation. His results are reproduced in figure 2.2. The upper curve is used to compare ordinary distillation with extraction while the lower one compares extractive distillation with extraction. If the relative volatility available in a distillation operation is 1.5, an extraction solvent yielding a value of at least 6.0 must be found if extraction is to be equal or lower in cost to ordinary distillation. For an extractive distillation process the equivalent required relative volatility is 2.0. Of course the final selection process requires a careful economic comparison for the specific case in question.

It thus stands to reason that if this study can produce a solvent suited to azeotropic or extractive distillation, significant cost advantages may be gained over the existing process. Equipment costs for the former types of processes are usually much lower than that for extraction. The relative volatilities reported by Quann and Tabak (1987:8) for the removal of butanone is in the order of 4 and that for 2-pentanone is in the order of 2. Heavier oxygenates such as hexanone was not considered in the study but a low value of 1-1.5 seems to be in line. Given the comparative values discussed above, it is almost assured that a process involving azeotropic or extractive distillation will be considerably cheaper than the liquid wash process.

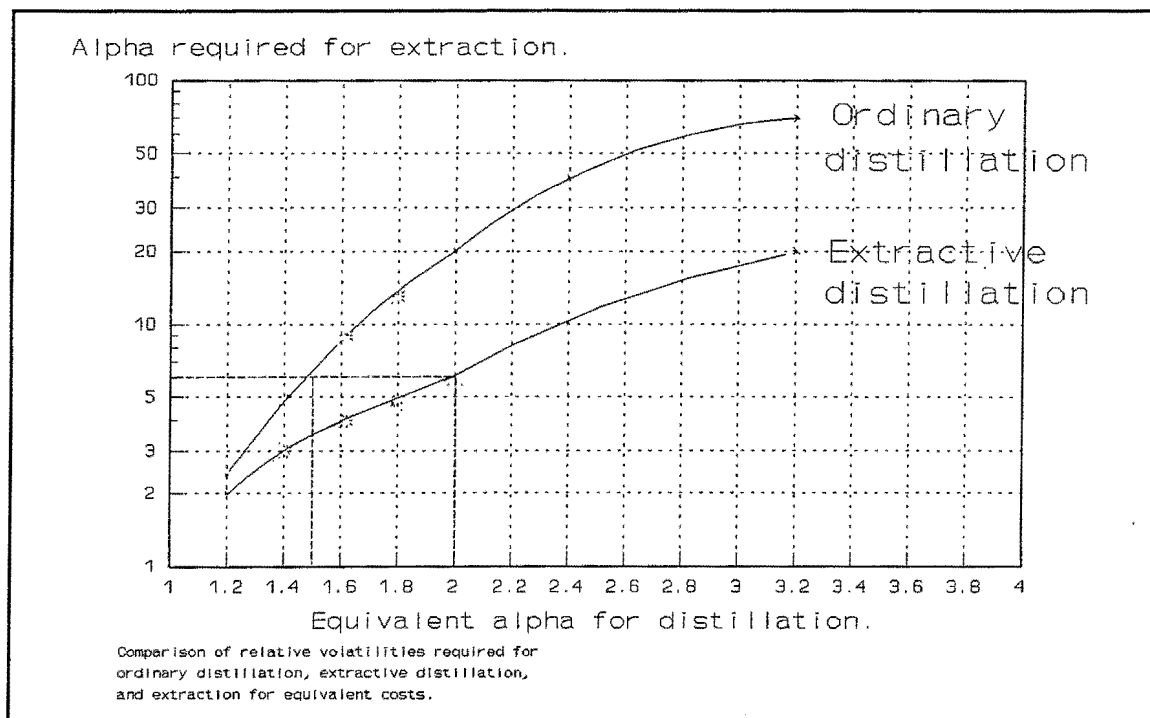


Figure 2.2: Relative costs.

Since the C9 and C10 streams are similar to the C8, results from this study may also shed light on these higher streams.