Effect of pH change on the vapour-liquid equilibria of n-butyric acid and water

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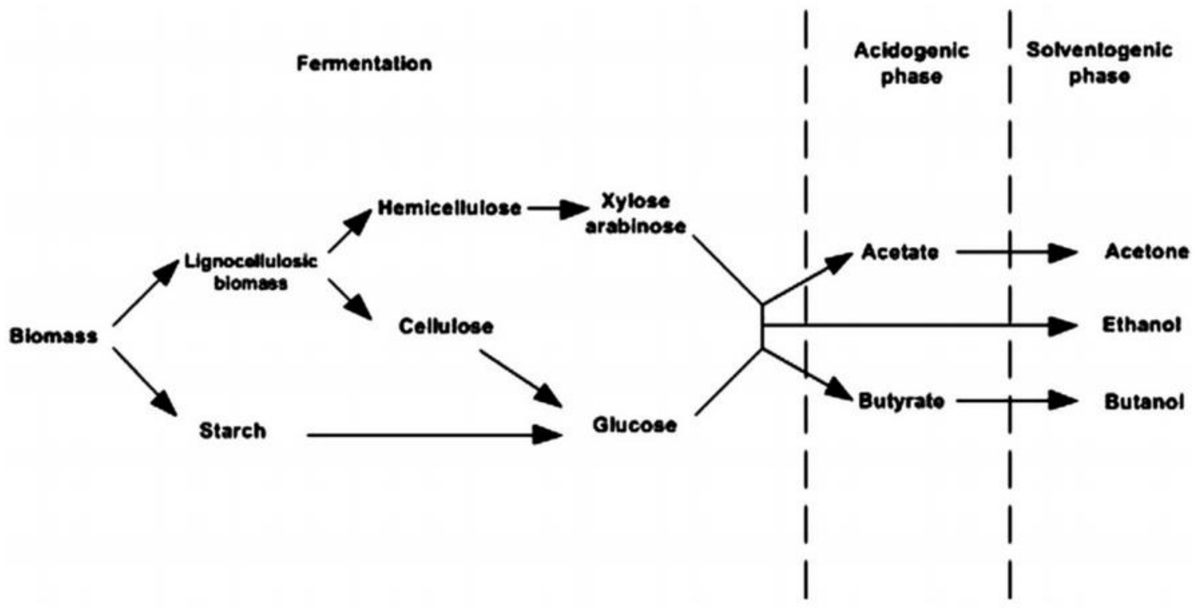
Abstract

The vapour-liquid equilibrium (VLE) of a binary system of n-butyric acid and water was studied. In terms of acid-base equilibria, weak acids have a low rate of dissociation (<1%) in solution. In the presence of a strong base, the amount of weak acid that dissociates is virtually equivalent to the amount of the base present in solution. The effect of changes in the dissociation of butyric acid on a solution's VLE was tested isobarically at 101.3 kPa to determine the relationship between the volatility of butyric acid and its conjugate base. Solutions of concentration between 0.5 and 2 mol/L of n-butyric acid and water were brought to their boiling point and the resulting vapour was condensed and recycled to the boiling solution until steady state was reached. The composition of n-butyric acid and water of the condensate and the solution were then measured and plotted on an x-y diagram to map the shift in volatility as n-butyric dissociation increased. Different VLE curves were obtained at different pH by the addition of sodium hydroxide base to progressively dissociate the amount of n-butyric acid tested.

Introduction

In recent years, issues concerning the unstable future of gasoline as a major source of energy have renewed interest in developing alternate fuels through economically and environmentally sustainable production methods.

The most promising alternative is bio-butanol, an alcohol with a longer hydrocarbon chain that causes it to be fairly nonpolar. This implies higher energy density, as well as better solubility within other hydrocarbon fuels than previously researched bio-ethanol.



Simplified product formation pathway by solventogenic *Clostridium* species.

The most common means of production is through Acetone-Butanol-Ethanol (ABE) Fermentation, using *Clostridium acetobutylicum*. The bacteria undergoes two distinct phases: production of acetic and butyric acid (acidogenesis) during rapid exponential growth, followed by production of acetone, butanol and ethanol (solventogenesis) when growth slows down.

Motivation

Excessive accumulation of acetic and butyric acid in the ABE fermentation broth can lead to 'acid crash', which is characterized by a failure of the bacteria to switch from acidogenic to solventogenic metabolism. For this reason, proper pH maintenance in the broth is important.

The recycling of residual sugars from fermentation plants require the removal of produced butyric acid to ensure process efficiency. Broths of varying pH have different proportions of butyric acid to butyrate (the former's conjugate base anion). Understanding the relative volatility of butyric acid in a controlled solution of water can give insight into its role in future separation techniques and their subsequent design.

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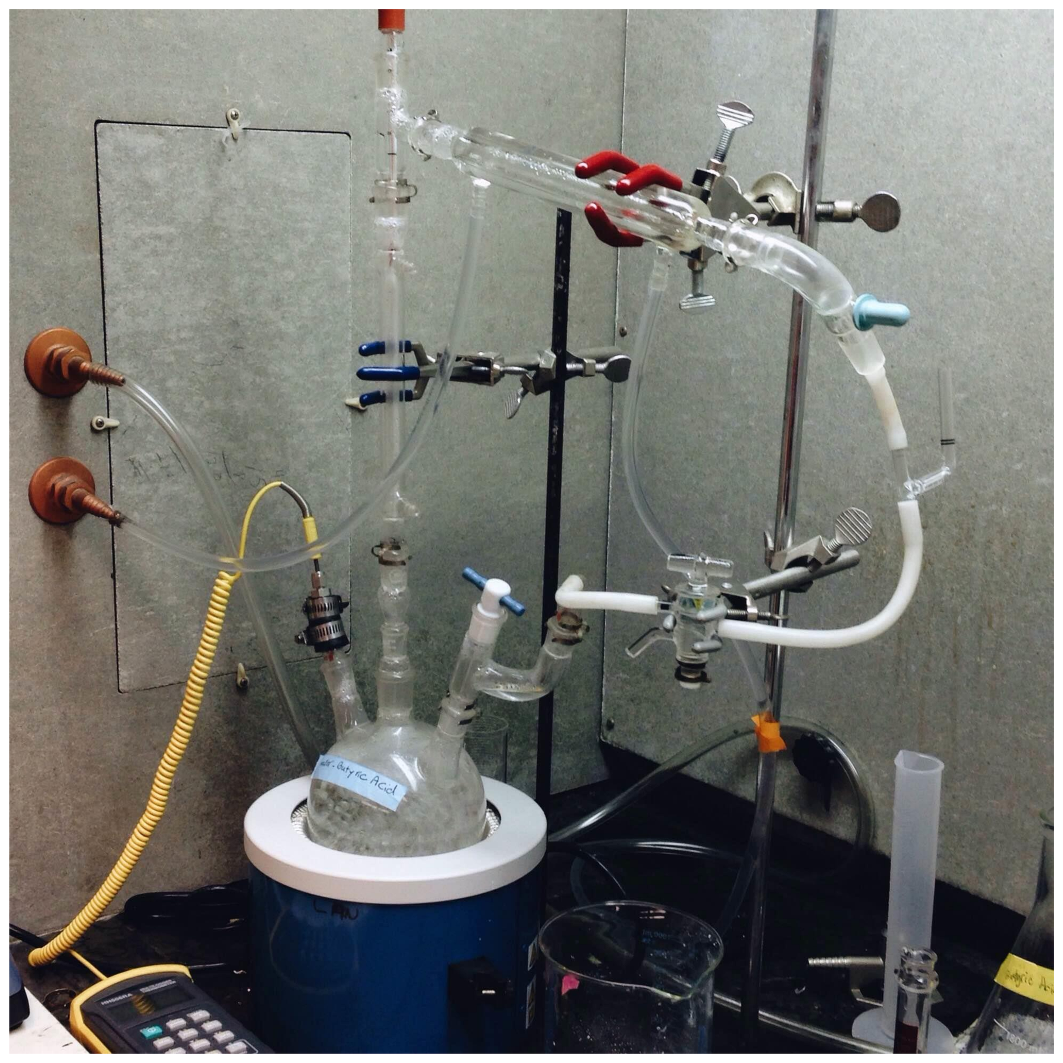
Methodology

The apparatus used for testing the VLE of n-butyric acid and water consisted of a boiler and a condenser circulating a 1 L solution of both components until equilibrium was reached. Three overall concentrations of butyric acid were tested: 2 mol/L (18.49%), 1 mol/L (9.24%) and 0.5 mol/L (4.62%).

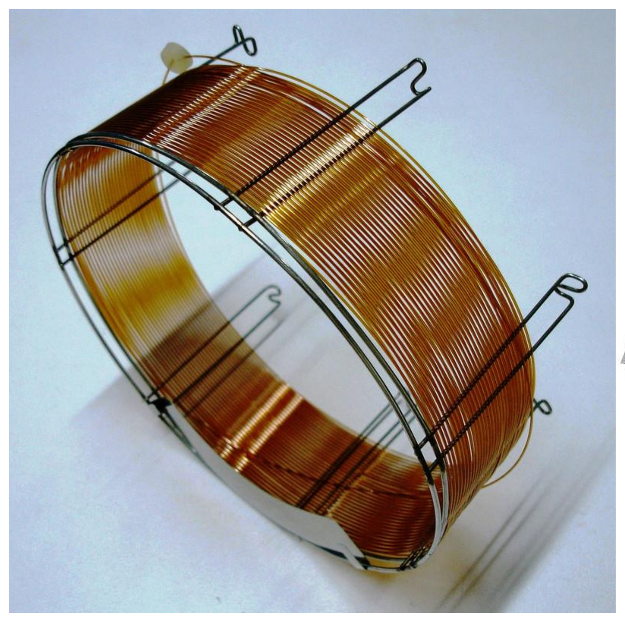


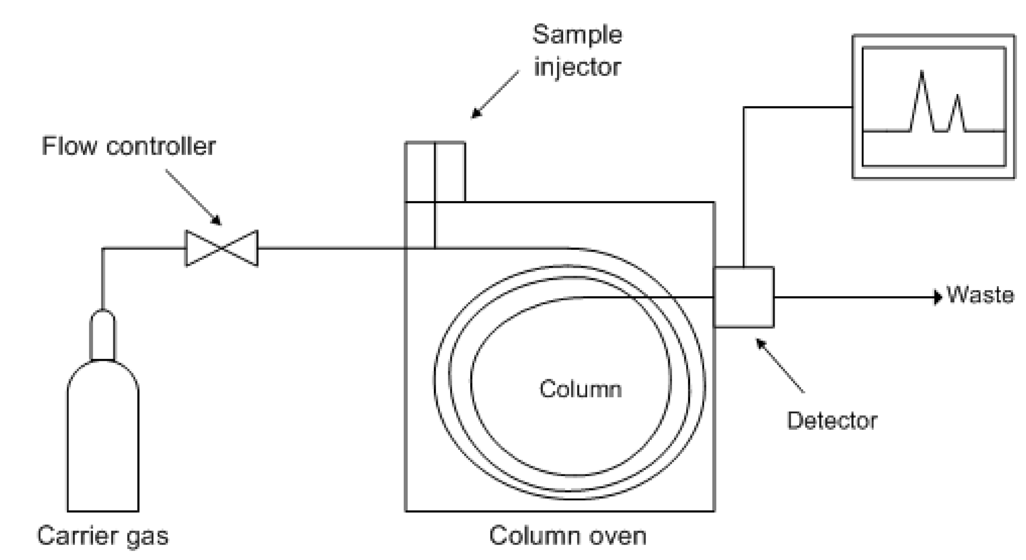
The pH of the solution was adjusted through a systematic addition of pure NaOH to progressively increase the percentage of butyric acid found in its dissociated form, butyrate:

$$CH_3CH_2CH_2{-}COOH + Na^+ + OH^- \rightarrow CH_3CH_2CH_2{-}COO^- + H_2O + Na^+$$

A solution with a higher pH will have a higher percentage of butyrate ions, reflecting the possible variations in concentration in a fermentation broth.

Gas Chromatography was used to analyze the resulting concentrations in the liquid and vapour phases of the equilibrium.





A SRI GC Model was connected to compressed air and hydrogen carrier gasses. When a microliter sample was injected into the GC, the mixture was ignited and would travel through the column to the detector. Peaks would arise in the recording software at sections of the column corresponding to specific components based on their chemical structure. A calibration line was created to link the area calculated under each peak with a tangible concentration of butyric acid in solution.

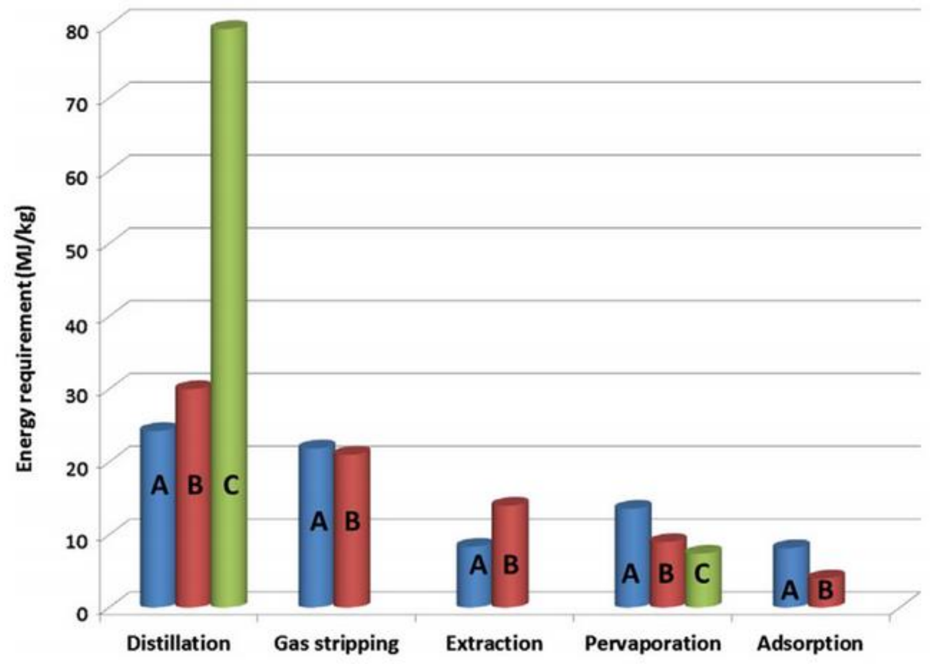
Conclusions

There are obstacles present in the use of gas chromatography to analyze concentrations in samples taken containing butyric acid and NaOH due to the ionic nature of the latter. NaOH can crystallize inside the column, thus obstructing the flow of gas through to the detector and damaging the adsorbent within. This renders current results inconsistent, and thus alternative analysis methods must be used.

A more robust option is High Performance Liquid Chromatography (HPLC), which uses a carrier liquid rather than a gas to flow through the adsorbent filled column. Changes in flowrate due to interaction between the sample's constituents and the adsorbent allow for identification of the concentration of each component present in the stream.

Further research applications

The need for adequate separation of butyric acid from ABE fermentation broths is closely connected to the need for isolation of produced butanol as well. ABE fermentation produces butanol efficiently, but in dilute quantities. The butanol must be purified out of the broth quickly to prevent toxicity to the *clostridium* bacteria, as well as in such method that is energy efficient enough to make the process economically viable.



Energy requirements for butanol separation from ABE broth

Adsorption and pervaporation were found to be among the most energy efficient separation techniques for butanol, both of which are currently being researched by Niloofar Abdehagh and Hoda Azimi at the University of Ottawa.

Pervaporation (Hoda Azimi)
This technique creates a vacuum on one side of a semi-permeable membrane, through which specific components of the fermentation can pass through by way of partial vaporization and later recovered through cold traps. Polydimethylsiloxane (PDMS) membrane are tested with additives to enhance selective permeability.

Adsorption (Niloofar Abdehagh)
This technique allows butanol from the fermentation to attach itself to a solid adsorbent, which can be later desorbed and regenerated with increased temperature. Initially, activated carbon was tested, but other options include resins and zeolites.

Acknowledgements

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