

HYPERBRANCHED POLYMERS IN ABSORPTION: EXPERIMENTAL CO₂ SOLUBILITIES

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Abstract

Oxidative coupling of methane (OCM) is an approach for the direct catalytic conversion of methane to higher hydrocarbons, which is currently being investigated at the Berlin Institute of Technology within the cluster of excellence UniCat (Unifying Concepts of Catalysis). Hereby, the conversion to ethylene is the major goal of the process. In the downstreaming process subsequent to the OCM reaction, a purification step takes place, where carbon dioxide has to be removed from the raw gas. This is done by chemical absorption using an aqueous amine solution, which can have several disadvantages such as a high energy demand for regeneration or solvent losses¹. However, it has been shown that hyperbranched polymers are promising candidates for gas absorbents with a high capacity for CO₂ and with large selectivities².

In this work, a commercially available hyperbranched polymer (Boltorn Perstorp) is investigated. The potential for its use as absorbent in the separation of CO₂ is evaluated by measuring solubilities. The results obtained are reported in terms of Henry constants within the temperature range of 283.15 to 303.15 K. In addition, the densities of the pure polymer or its solution with ethanol are measured in the same temperature range.

Keywords: absorption, carbon dioxide, OCM, hyperbranched polymers

1. Introduction

Oxidative coupling of methane (OCM) is an approach for the direct catalytic conversion of methane to higher hydrocarbons, which is reaching widespread attraction among various research groups in the last decade. The conversion to ethylene is the major goal of the process. OCM is a surface induced gas phase reaction and its overall yield is still limited up to 30%. Besides new catalysts, a concept for an integrated downstream process is necessary to overcome this limitation³.

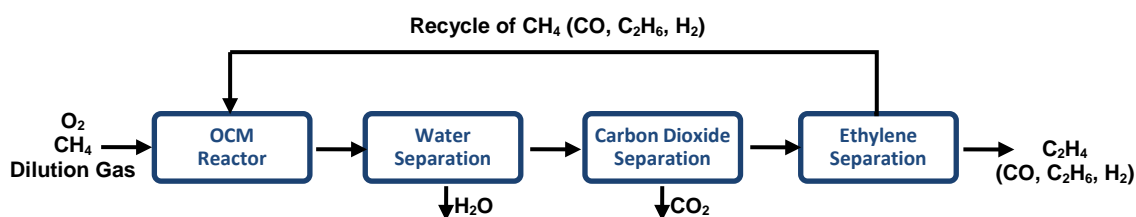


Figure 1. Process flow diagram of the OCM process³

Various processes for the OCM have been proposed so far, such as the OXCO process, the UCC process, the ARCO process, the Suzuki process, the Turek-Schwittay process or the Co-Generation process⁴. All of them have in common that the product separation under high pressure and the recycling of unreacted methane is of most importance for the process economics. Because of its current low yield and challenges for an efficient downstream process, OCM has not been applied in the industry yet. Therefore, a miniplant has been built at the Chair of Process Dynamics and Operation of the Berlin Institute of Technology, where fundamental studies of process alternatives and the effect of recycles and efficiencies of each process unit are being investigated. Figure 2 shows the generalized layout of the miniplant.

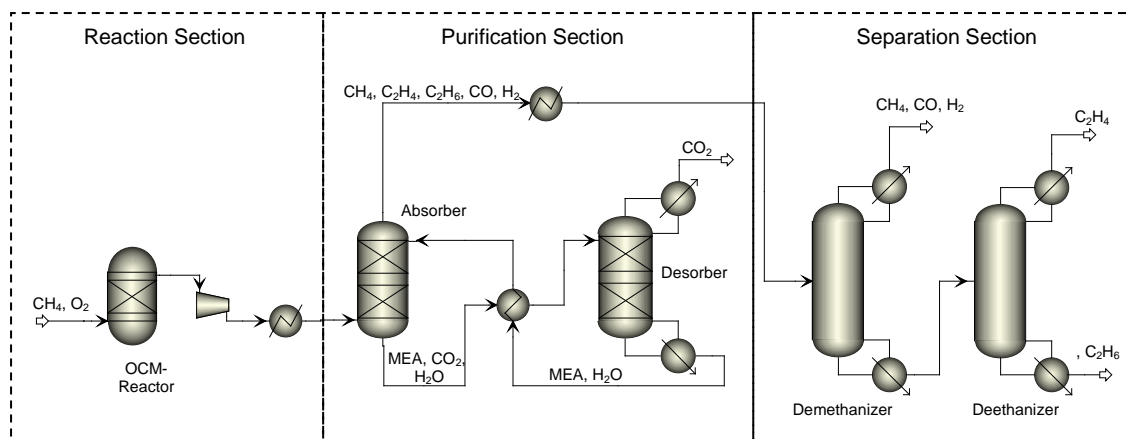


Figure 2. Simplified process flow diagram of the OCM⁵

For process synthesis, the whole OCM process is divided into three general sections: subsequent to the reaction, a purification step takes place, where carbon dioxide has to be removed from the raw gas completely. Finally, in the separation section, the desired reaction product, ethylene, is being separated from all other components, which may be recycled to the reaction section again. Currently, there is the process concept of using carbon dioxide as an inert gas for dilution in the OCM reactor. Thus, the carbon dioxide removal is an even more important step of the downstream process, and therefore, is being focused on.

Different separation techniques have been evaluated for the miniplant, such as adsorption, membranes, absorption and cryogenic separation techniques. Hereby, absorption was found to be most suitable for the given task. Absorption of carbon dioxide is well developed and industrial available. Physical absorption processes like the UOP Selexol® or the Lurgi Rectisol® processes are known, which use dimethyl ether and cold methanol, respectively. Due to a nearly similar solubility of the product and the carbon dioxide in the liquid, those physical absorption processes cause high product losses of more than 30 vol%. Therefore, only chemical solvents like Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA) or a mixture of them have been considered so far in the OCM miniplant. These chemicals are used in amine scrubbing processes like the aMDEA® process in different concentration ranges⁶. Standalone rigorous simulations for the absorption process of the miniplant were carried out in Aspen Plus®. As scrubbing liquids, 15 wt% MEA and 30 wt% MDEA solution were compared, where neither MEA nor MDEA as solvent could remove the carbon dioxide totally in a standalone absorption process for the given conditions. As a result, a hybrid membrane amine process for the removal of carbon dioxide in the product stream was proposed, where a two stage membrane system has been combined with an absorption column to form a hybrid process⁶.

In this work, hyperbranched polymers are being investigated as an alternative for absorbents for carbon dioxide, since they have shown being promising candidates for gas absorbents with a high capacity for CO_2 and with large selectivities².

2. Hyperbranched polymers

Currently, four major classes of polymers can be distinguished in accordance with their properties and polymeric architecture. Dendritic polymers herein represent the fourth class and are highly branched globular macromolecules. They can be subdivided into three subsets that are related to the degree of structural control, i.e. random hyperbranched polymers, dendrigraft polymers, and dendrimers⁸ (see Figure 3).

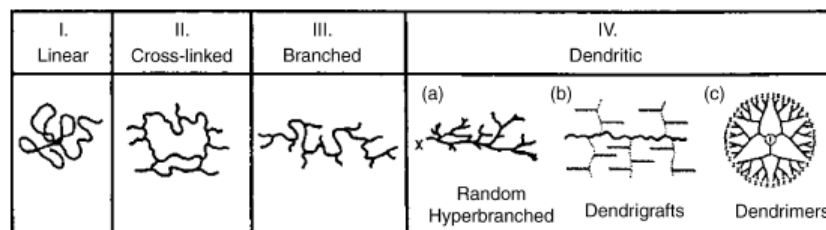


Figure 3. Classes of macromolecules'

Dendrimers and hyperbranched polymers have attracted considerable and increasing interest during recent years. They resemble each other in that they are both polymerized from monomers with mixed reactivities, commonly denoted A₂B or A₃B monomers, thus, giving branched structures with exponential growth, in both end-group functionalities and molecular weights. Their properties differ strongly from those of linear polymers of the same molar mass (less flexibility, lower entanglement degree, a significant chain-end effect, lower viscosity in solution and in the molten state, high solubility in common solvents, a different relationship between hydrodynamic volume and molar mass, and a different origin of the glass transition temperature)⁹.

Dendrimers show a well defined, monodisperse, perfectly branched structure and have a large number of functional end groups¹⁰. Each generation is built up step-by-step with many protection and deprotection synthetic and purification steps, which requires absolute control of all synthesis steps and makes large-scale production difficult and hence expensive. However, many applications do not require structural perfection. Therefore, using hyperbranched polymers can circumvent this major drawback of dendrimers¹¹.

Unlike dendrimers, randomly branched hyperbranched polymers with similar properties can be easily synthesized via one-step reactions and therefore represent economically promising products also for large-scale industrial applications. At room temperature, many branched polymers are liquids above their glass temperatures and exhibit low viscosities in the pure state as well as in solution due to the absence of chain entanglement. Potential applications of hyperbranched polymers range from the use as selective solvents in distillation of azeotropic mixtures or extraction to the control of flow characteristics, as well as the use as drug delivery system and many more.

Boltorn® dendritic polymer

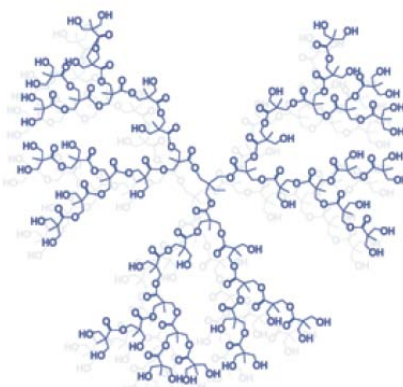


Figure 4. Boltorn molecule by Perstorp Group (Sweden)

In this work, the hyperbranched polyester/ether polyol Boltorn® P500 by Perstorp is introduced to carbon dioxide absorption. Its molecular structure is shown in Figure 4. Boltorn® P500 was chosen because of its high average hydroxyl functionality and, compared to similar polymers, low viscosity. Still, this has to be considered as a first step followed by more detailed investigations on different commercially available polymers and also on tailor-made polymers, which could be optimized in terms of capacity, selectivity, and stability with regard to economic demands.

3. Measurements and Calculation

3.1 Experimental Setup and Procedure

Figure 5 shows a schematic diagram of the experimental setup that was used in this work. A maximum of two equilibrium cells (8) can be measured simultaneously, each having a volume of 80ml. They are provided with a magnetic stirrer (9) and placed inside a water thermostat (11) with a temperature range of 283-363 K. The cell temperatures are determined with a resistance thermometer (Pt 100) in the water bath. The cells are connected via a valve and a quick connection to the gas systems (3) (each 135ml) which contain the solute and each are connected to a pressure sensor. The maximum pressure that can be applied is up to 1.2 bar. The temperature within the gas systems is measured with a resistance thermometer (Pt 100). The gas is fed from a reservoir (1) to the system. The cells and the gas systems are attached to a vacuum pump (19).

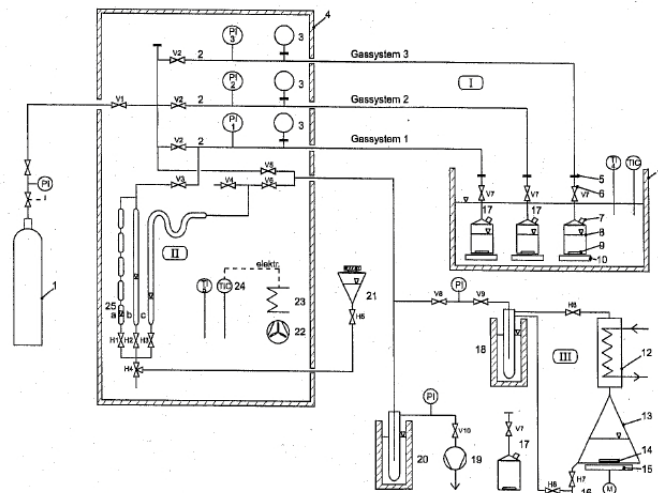


Figure 5. Schematic diagram of the gas solubility apparatus: (1) CO₂ supply; (3) gas reservoir; (4) gas room; (8) equilibrium cell; (9) magnetic stirrer; (11) water thermostat; (19) vacuum pump; (20) cooling trap; (23) electrical heating

The degassed solvent (liquid polymer or polymer solution) is filled into the equilibrium cell at constant temperature and stirred continuously. After evacuating the system and the cell, the valve between the cell and the system is closed and the gas is fed from the reservoir (1) into the gas system. Then, the gas is admitted into the cell and absorbed until equilibrium is reached (i.e. a constant pressure is observed). Due to usually higher solubilities at lower temperatures, it is best to start with the highest temperature and decrease it in the course of the experiments. The time of equilibration of the whole system (system + cell) depends on the viscosity of the solvent and the solubility and takes roughly 90 minutes. For reproducibility, experiments were repeated three times with two equilibrium cells. Densities of the polymer and its solutions with ethanol were measured in the corresponding temperatures range using a pycnometer with a volume of 25ml.

3.2 Calculation of the Henry coefficients

In order to decrease the viscosity of the solvent, the polymer was mixed with ethanol (resulting solution: 30% weight fraction of ethanol). Assuming that no polymer is in the gas phase, the amount of absorbed CO₂ can be determined iteratively by PVT-calculations of the gas system and the gas in the cell, and subsequently solving mass balances:

$$n_{CO_2}^{abs} = n_{CO_2,0}^{gas\ system} - n_{CO_2,1}^{gas\ system} - \left(V_{cell} - \frac{m_{ethanol} + m_{polymer} + \tilde{M}_{CO_2} \cdot n_{CO_2,cell}^{abs}}{\rho_{CO_2+polymer+ethanol}^L} \right) \frac{1}{v_{CO_2+ethanol,cell}^G} \quad (1)$$

The molar amount of CO₂ in the gas system as well as the molar volume of the gas phase in the cell are calculated using the Soave-Redlich-Kwong equation of state (SRK). The density of the liquid phase was found to be almost independent of the amount of CO₂ absorbed. Therefore, only the density of the pure solvent mixture is considered. The mass-fraction is then easily achieved by:

$$w_{CO_2}^{abs} = \left(\frac{\tilde{M}_{CO_2} \cdot n_{CO_2,cell}^{abs}}{\tilde{M}_{CO_2} \cdot n_{CO_2,cell}^{abs} + m_{ethanol} + m_{polymer}} \right) \quad (2)$$

Since the mass-fraction () and the pressure () are low, the Poynting correction and activity coefficient can be neglected¹² such that the mass-fraction based Henry coefficient can be calculated by

$$H_{CO_2,polymer} = \frac{y_{CO_2} \cdot P}{w_{CO_2}^{abs}} \quad (3)$$

4. Results and conclusions

Figure 6 shows the results of the density measurements as a basis for the solubility calculations for both Boltorn® P500 + ethanol solution and pure ethanol. The latter show also good agreement with values from literature¹³.

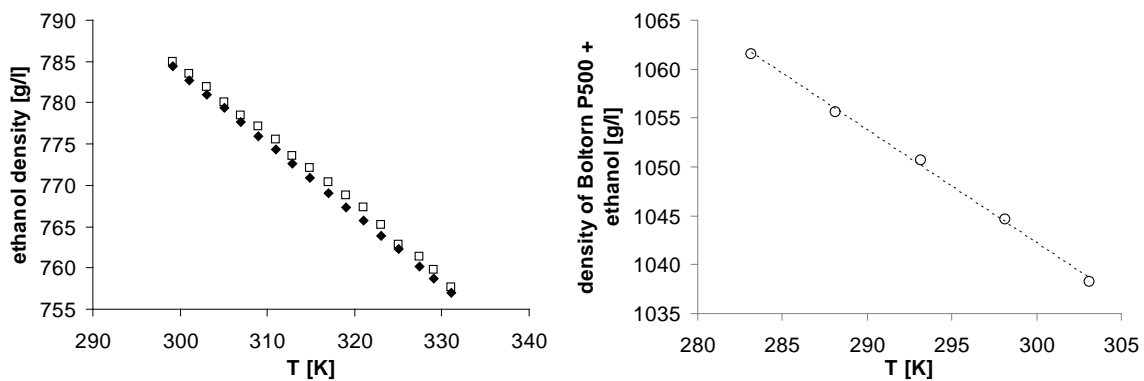


Figure 6. Densities of ethanol (□ measurements, ♦ literature¹³) and polymer solution (○)

In Figure 7, the calculated mass-fraction based Henry coefficients of CO₂ in the respective solvent can be seen. Again, pure ethanol was measured as reference case.

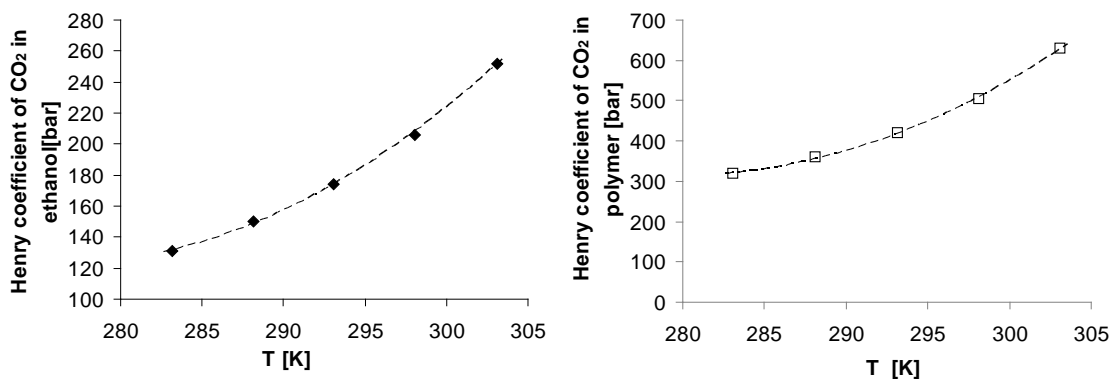


Figure 7. Mass-fraction based Henry coefficients of CO₂ in ethanol (♦) and in polymer solution (□)

In addition to the thermodynamic experiments, kinetic investigations on the CO₂ absorption behavior in hyperbranched polymers are still on the way. The kinetics play also an important role in absorption but are not discussed in this work.

Moreover, simulation studies using Aspen® will be presented to validate the potential of hyperbranched polymers in removing CO₂. Furthermore, a miniplant is being built for the whole OCM downstreaming process within the UniCat project¹⁴. Thus, suitable hyperbranched polymers will be investigated further on a larger scale in the downstreaming miniplant.

Acknowledgements

The authors acknowledge support from the Cluster of Excellence "Unifying Concepts in Catalysis" coordinated by the Technische Universität Berlin and funded by the German Research Foundation - Deutsche Forschungsgemeinschaft. We would also like to thank Perstorp for providing us with a sample of Boltorn® P500.

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