

DEVELOPMENT OF TASK SPECIFIC HYPERBRANCHED POLYMERS FOR THE SEPARATION OF CARBON DIOXIDE: CARBON CAPTURE AND BIOGAS UPGRADE

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Abstract

Hyperbranched polymers are a group of components which have been successfully used in several applications in chemical engineering. The structure of these molecules is very flexible and can be tailored by changing functional groups or the repetitive unit.

In this work the application of hyperbranched polymer for the upgrade of biogas is investigated. To limit the large numbers of possible polymer structures the a-priori predictive method COSMO-RS is used. The goal was to find the most suited molecules for the separation of carbon dioxide and methane. These optimized components are synthesized and used for further investigation. Results of the a-priori calculations and comparison with measured data are presented. Also the requirements for a solvent for the biogas upgrade and the relation to the chemical structure of a hyperbranched polymer are shown.

Keywords: hyperbranched polymers, carbon dioxide capture, task specific solvent, COSMO-RS

1. Introduction

In the past years the discussion about climate problematic and the necessary consequences has gained a lot of interest. The use of renewable sources of energy is always named as an important part of the solution in this context. One of the possible sources is biogas. The energy can be provided independently from day time or weather conditions. In the year 2006 an amount of 4898.9 kilotons of oil equivalent biogas was produced in the EU25¹. In Germany in the year 2008 4000 biogas plants were installed, which had a capacity of 1400 MW electrical power. For 2009 another 780 plants and an overall power of 1600 MW is prognosticated².

The gas itself is the product of the fermentation of raw materials like food waste or animal droppings. It is produced locally, for example at a farm, where the raw materials for the fermentation can easily be collected. For the further utilization it can be fed in the public natural gas network and used as fuel gas for cogeneration in a gas power plant. For this feeding the biogas composition has to fulfill several legal regularities. This refers mainly to the content of methane, carbon dioxide and hydrogen sulfide. The average gas composition of biogas and the requirements for the input in the gas network are collected in table 1:

Table 1. Gas composition and requirements for input in gas network for biogas

Component	Biogas composition	Requirement
Methane	55-70 vol-%	> 97 vol-%
Carbone dioxide	30-45 vol-%	< 6 vol-%
Hydrogen sulfide	< 1000 mg/m ³	< 5 mg/Nm ³
Water	saturated	< dew point
Caloric value	6-7.5 kWh/m ³	8.4-13.1 kWh/Nm ³

For upgrading the raw biogas there are several methods applied in industry. A common possibility to clean the hydrogen sulfide is the adsorption on activated carbon. The water can be removed for

example by adsorbing it to silica gel. The carbon dioxide can be removed either by adsorptive or absorptive processes. As absorbents solutions of monoethanolamines (MEA) are often used. They are forming carbamates with CO₂, which have to be regenerated at high temperatures in a desorption step. This makes the process expensive and energetically inefficient. The solvent may be deactivated by forming heat-stable salts with oxygen. Due to their finite vapor pressure some absorbent is also lost via the vapor phase in the methane and the carbon dioxide flow.

In this work hyperbranched polymers (hypPol) are investigated as possible solvents for the absorption. They have a negligible vapor pressure, which prevents the loss of solvent via the gas phase. Many hypPol are environmentally and personally not harmful. The structure can be tailored to reach a high selectivity for carbon dioxide. The gas should physically absorb to reduce the energy consumption for desorption. The solvent should also be inert to any other raw gas component to prevent solvent deactivation.

2. Theory

2.1 Conductor-like Screening Model for Real Solvents COSMO-RS

The model COSMO-RS was developed by Klamt and introduced to chemical engineering by Arlt^{3,4}. The geometry of any molecule is created in vacuum based on a quantum chemical approach. The next step is the calculation of the screening charge density by the density functional theory (DFT). The continuum model COSMO is used, in which the molecule is considered to be surrounded by an ideal conductor (value of the dielectric constant $\epsilon = \infty$). The result of this calculation is the so called σ -profile. In figure 1 on the left a water molecule is shown as an example. The color symbolizes the electron density distribution. With a statistical thermodynamics approach (COSMO-RS), the chemical potential of a component in a mixture can be calculated from this σ -profile (see figure 1, right). Further thermodynamic properties like the gas solubility can be derivate from this chemical potential. This method was applied successfully to various applications in chemical engineering and also to hyperbranched polymers⁵⁻⁷.

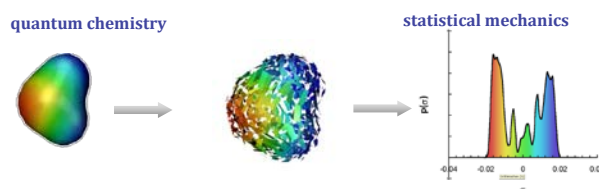


Figure 1. Procedure of the quantum chemical method COSMO-RS

2.2 Hyperbranched Polymers

Macromolecules are known in the field of chemistry and chemical engineering for a long time. According to Staudinger et al. the field of polymer science can be described by the two architectural classes of linear and crosslinked structure⁸. In figure 2 typical structures for branched polymers are shown:

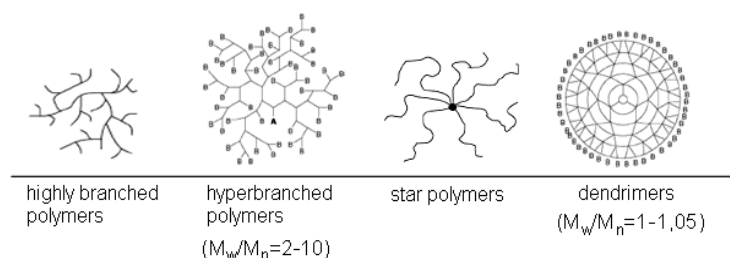


Figure 2. Structures of branched polymers (adapted from Prof. B. Voit⁹)

They distinguish in the mechanism of growth during the synthesis. This leads to a larger molecular mass distribution. A monodisperse polymer is achieved for dendritic molecules. Hyperbranched polymers are very polydisperse. Due to an easier route of synthesis for these polymers the price is much lower in comparison to dendrimers but the thermophysical properties are similar. A negligible vapor pressure prevents the loss of solvent with the vapor phase. The structure of a hyperbranched polymer can be made up of different building blocks. The functional groups can also be modified during or after the synthesis. The polymer structure can thereby be tuned specifically and the thermophysical properties be tailored for different applications. Recently, hyperbranched polymers have been used in various operations in chemical engineering^{9,10}. In this work a-priori calculation methods were used to suggest polymer structures for the separation of carbon dioxide and methane.

3. Method

With COSMO-RS it is possible to calculate thermodynamic properties from the molecular structure. For large molecules with a total number of atoms of bigger than 500 the DFT-calculations take a long time and errors may occur. A possibility to avoid these problems is the use of so called meta-files in COSMO-RS. The molecule is subdivided into smaller parts, which can be optimized in the DFT-calculation separately. For the computation of the thermodynamic properties these files can be rearranged in meta-files. In these meta-files the included parts are considered as one big molecule. The subdivision of the molecules and the optimization step can be done in various ways. The results from these calculations are compared with experimental data¹¹ and an approach to model hyperbranched polymers is developed.

This approach in COSMO-RS is used to evaluate the dependence of the polymer structure and its thermodynamic properties. The building blocks, the molecular weight and the functionalization are varied to find their influence on the

- solubility of carbon dioxide
- solubility of methane
- selectivity for carbon dioxide
- absorption enthalpy (see equation 1)

From these results the structure for novel hyperbranched polymers that are suited for biogas upgrade are deduced. They are synthesized in the laboratory and the gas solubility of carbon dioxide and methane is measured. From solubility measurements the solvent loading can be calculated. In figure 3 the solvent loadings at 313.15 K of three different hyperbranched polymers are plotted in comparison to the loading of MEA. The loading is referred to the pure solvent without considering the water content. The polymers show physical solution behavior, the loading is increasing proportional to the partial pressure. The typical partial pressure of CO₂ in raw biogas is 0.5 bar, which is represented by the dotted black line in figure 3. At this pressure the molar loading in a PAMAM solution is higher than in MEA.

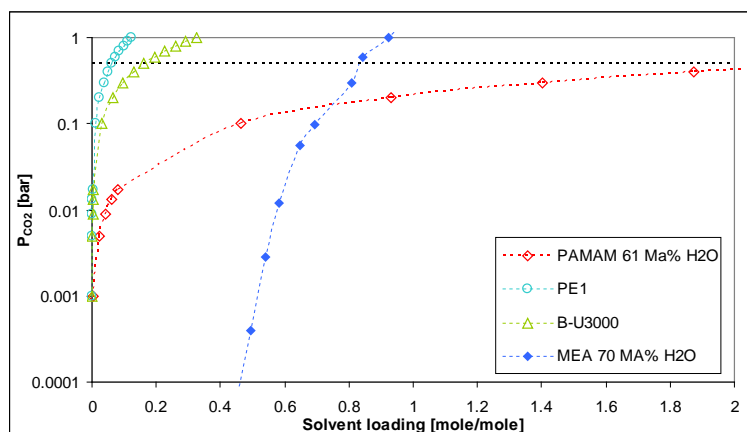


Figure 3. Vapor-liquid equilibrium of CO₂ in aqueous PAMAM solution, hyperbranched Polyether PE1, hyperbranched Polyester B-U3000 and aqueous MEA solution at 313.15 K¹¹

Due to their high molecular mass, however, the required mass flow for the absorption is higher. In figure 4 the required mass flow of three different hyperbranched polymers are compared to the mass flow of a MEA solution. In the example given, carbon dioxide should be separated from an overall feed flow of 200 m³/d. The concentration of CO₂ should be reduced from 50 vol-% to 3 vol-%. The required mass flow for PAMAM is ten times bigger than the mass flow for MEA, the required mass flow for PE1 and B-U3000 even more than 100 times bigger than the mass flow for MEA. This fact may influence the required equipment size.

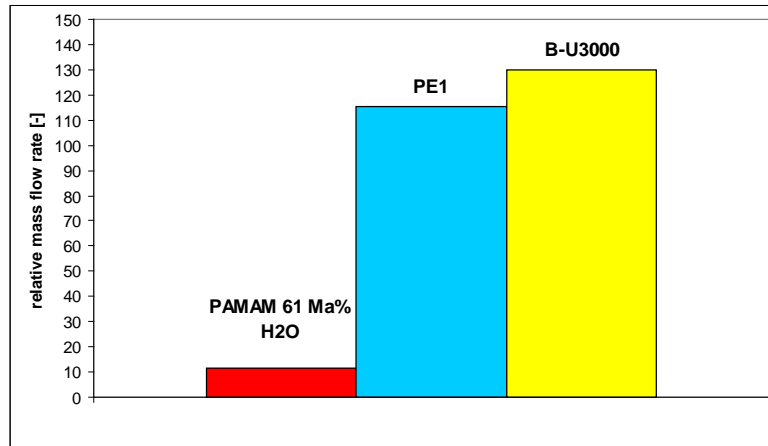


Figure 4. Required mass flow of solvent in relation to an aqueous MEA solution

The absorption enthalpy of carbon dioxide at infinite dilution $\Delta h_{\infty,i}^{GL}$ can be calculated from the temperature dependence of the gas solubility, which can be written in terms of the Henry constant $H_{i,j}$ (see equation 1):

$$\left(\frac{\partial \ln H_{i,j}}{\partial \left(\frac{1}{T} \right)} \right)_{P,x \rightarrow 0} = \frac{\Delta h_{\infty,i}^{GL}}{R} \quad (1)$$

A lower absorption enthalpy means also a lower energy that is necessary for the desorption of carbon dioxide and the regeneration of the solvent. In figure 5 the results for the absorption enthalpy of carbon dioxide in different solvents are shown. The solution of 30 weight-percent MEA in water as a reference for the present process is compared with a solution of the dendritic polymer PAMAM, a branched Polyether 1, two linear Polyether 2 and 3 with different molecular weights and the hyperbranched polyester B-U3000. From this plot it can be seen that the absorption enthalpy of polymers is significant lower than in the MEA-solution. This shows the high potential to reduce the energy consumption by using novel solvents.

4. Conclusions

It is possible to tailor solvents suited for biogas upgrade (gas solubility of carbon dioxide and methane) with the a-priori calculation method COSMO-RS. An approach to calculate large molecules like hyperbranched polymers is demonstrated. The best candidates are synthesized and the gas solubilities are measured for comparison. Several parameters like the solvent loading and the absorption enthalpy must be evaluated to find a suited novel solvent for the absorption with an overall economical optimum.

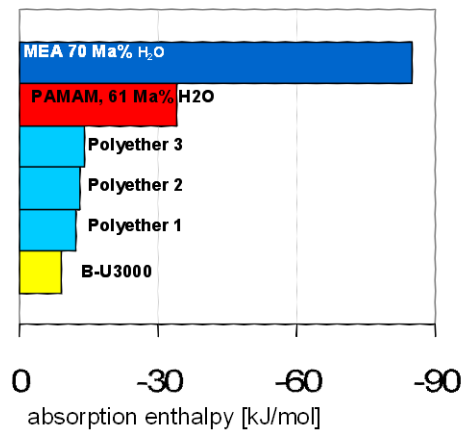


Figure 5. Absorption enthalpy of carbon dioxide in different solvents¹¹

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