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Charge air separation for the reduction of marine diesel engine emissions by means of poly(vinyl trimethylsilane) membranes

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Poly(vinyl trimethylsilane) (PVTMS) is well-known for almost half a century to be a highly permeable glassy polymer, which shows an oxygen permeability in the range of 50 Barrer at good O_2/N_2 selectivity of about 4. PVTMS was the first polymer, which was industrially produced solely as a membrane material for the production of integral asymmetric gas separation membranes. These membranes, which were produced in the Soviet Union and France showed oxygen permeances up to 0.4 $m^3*m^{-2}*h^{-1}*bar^{-1}$, which is equal to approx. 145 GPU. The industrial production of PVTMS was unfortunately stopped with the collapse of the USSR [1, 2]. Present-day multi-layer membranes produced as thin film composites at the Institute of Polymer Research of HZG enable the use of experimental and tailor made polymers. The polymer consumption for the forming of the selective layer, which can be thinner than 100 nm, is less than 100 $mg*m^{-2}$ and a pilot scale membrane production is possible with only few grams of polymer. This was another reason to restart PVTMS synthesis especially for the use as air separation membrane material.

Quite often processes of air separation do not demand for highest permeances and selectivities. Medium selective membranes combined with reasonable oxygen permeances show economic advantages for selected processes. One example is the enrichment of nitrogen from 79.1 vol.-% to about 84 vol.-% for the reduction of nitrogen oxide emissions of diesel engines [3, 4].

In a joint project with WTZ Roßlau – a private research enterprise specialized in the field of energy conversion and engine technology – the application of membrane separation for the nitrogen enrichment in the charge air of marine diesel engines was investigated. An industrial scale membrane module was installed in the charge air pipe of a research diesel engine with almost 100 kW output. The focus of the research is on optimization of the membrane module, engine operation and engine control – and in the end to gain information about reliability and economics of this process.

The backgrounds of this project are new regulations of the International Marine Organization IMO, which limit the emissions of marine engines. On one hand shipping is the most effective mode of transportation besides road traffic and aviation. The contribution of CO_2 emission is only 15% - taking into account that 90% of global trade in transported tonnes per mile are handled by ships – the impression is even more positive. On the other hand the portion of ship emissions of nitrogen oxides, particulates and sulphur dioxide ranges from 42 to 72%. While the reason for the emission of nitrogen oxides is the diesel process, the use of strongly sulphurous fuels causes large emissions of sulphur dioxide and particles. In selected sea areas and harbours the picture gets even worse. Increased nitrogen oxide concentrations can be observed along main shipping routes. An older study came to the conclusion that the portions of ship emissions of nitrogen oxides were 75% and 99% of sulphur dioxide in the harbour of Lübeck-Travemünde.

The need to reduce ship emissions was recognized by the International Marine Organization (IMO). Limitations of the emission of nitrogen oxides by marine diesel engines from the year 2000 onwards (IMO I) were established, which were met by improving the state of the art in engine technology at that time. A more drastic reduction was adopted in a stage model in the year 2008 - compared to IMO I the nitrogen oxide limit should be reduced by approx. 20 % in the year 2011 (IMO II) and approx. 80 % in the year 2016 (IMO III - applicable in Emission Control Areas (ECA), which mainly could be found in coastal areas and harbours).

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For a reduction of NO_x by 80 to 90% additional methods like exhaust-gas recirculation (EGR), catalytic exhaust gas reduction, gas operation of the engine or charge air separation by membranes are required.

The reduction of nitrogen oxides by increasing of the portion of inert gas in the charge air by means of gas-separating membranes has been investigated on a research diesel engine at WTZ Roßlau. By enriching the charge air with nitrogen to about 84%, the emission of nitrogen oxides can be decreased by more than 80 %, whereas the filter smoke number strongly increases. By increasing the swirl and optimization of the injection it is possible to meet IMO III limits for nitrogen oxides with invisible smoke and slightly improved fuel consumption (see Fig. 1). The introduction of this method requires for high charge air pressures, powerful injection systems and highly efficient membranes [5].

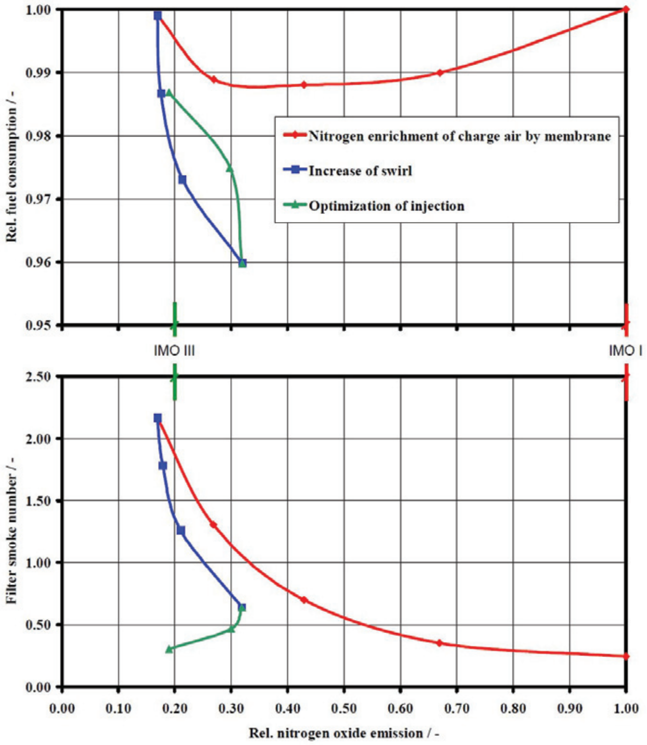

Figure 1: NO_x reduction by engine optimization

As already reported by S. Rangou [6] PVTMS and block copolymers of vinyl trimethylsilane with isoprene were synthesized by anionic polymerization at the Institute of Polymer Research of HZG. Thin film composite membranes were formed on top of dense supporting layers. Figure 2 shows the simple resistance model calculation assuming an oxygen permeance of the supporting layer in the range of $5\ m^3*m^{-2}*h^{-1}*bar^{-1}$ at O_2/N_2 selectivity of 2.25 as a red line. The included points are the average test results of two different membrane batches prepared in m^2-scale using two different coating solution concentrations. The points are very close to the theoretical line, which indicates almost perfect layer formation of 115 nm for 0.3 % PVTMS polymer concentration and 75 nm respectively for the lower concentration.

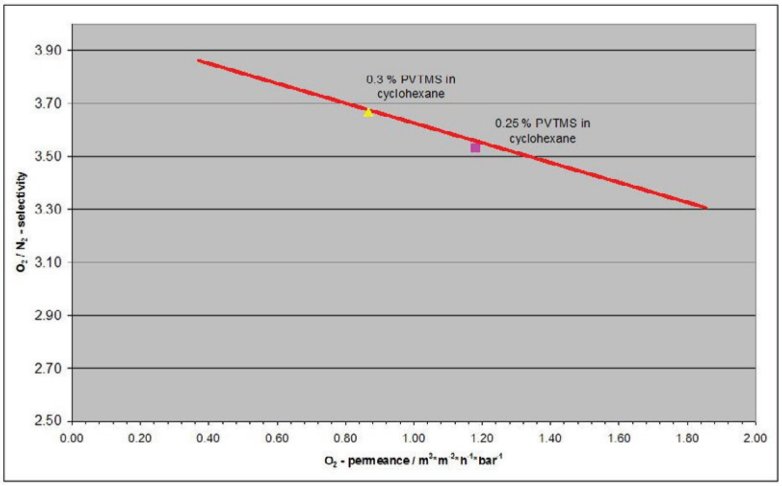

Figure 2: Resistance model calculation and test results

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