



CONCEPTUAL PROCESSES FOR ZEOLITE MEMBRANE BASED HYDROISOMERIZATION OF LIGHT ALKANES

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ABSTRACT

A zeolite membrane reactor concept for the hydroisomerization of n-hexane was applied experimentally. The results indicate separation selectivities with factors close to 20 for n-, mono- and dibranched components in a gas mixture, as well as n-hexane conversions up to equilibrium values. The research octane number calculated for the product stream of the different experiments indicates numbers as high as 85. For the hydroisomerization of C₇ alkanes, a concept of two reactors and a zeolite membrane was proposed and an industrial scale process was simulated. A high octane number product containing tribranched, and a part of dibranched, C₇ isomers is predicted. Although the product yield was calculated to be only 24% of the process feed, there was an improvement in a research octane number from 57 for the feed to 92 for the product. Both processes show that the application of zeolite membranes in the hydroisomerization of light alkanes can result in an octane number higher than in the "state of the art" processes. The membrane unit, however, is the main cost driver of the processes, thus, the economical feasibility of industrial scale light alkanes hydroisomerization processes using zeolite membranes is restricted to its further commercial development.

Keywords: Zeolite membrane; Hydroisomerization; Separations; Conceptual process;
Hexane; Heptane

INTRODUCTION

Environmental restrictions imposed on gasoline resulted in the removal of lead compounds and in limits for toxic compounds such as

aromatics, in particular benzene, olefins, and sulphur containing components. Reformulation in gasoline composition is occurring worldwide. In the European Union the limits placed on gasoline composition for the year 2000 are sulphur levels of 150 ppm, 18% olefins, 1% benzene, 42% aromatics and 2.7% oxygen. For the year 2005 sulphur must be further reduced to 50 ppm and aromatics to 35% [1]. As the octane boosters such as lead, oxygen containing components (MTBE, ETBE), and aromatics are removed or reduced in the gasoline pool, hydroisomerization of straight chain alkanes is becoming extremely important as an alternative for octane upgrading, since the highly branched isomer products formed have very high research octane number (RON). Thus, they are the only alternative that is acceptable as octane booster. Hydroisomerization of light alkanes such as C_5 and C_6 is already applied industrially, yet, the use of membrane reactors as the hydroisomerization of C_7 might still offer new and promising industrial features. In this work, a preliminary study is reported in which octane upgrading capacity higher than that found in the current state of the art is targeted by using zeolite membrane reactors and zeolite membranes for the hydroisomerization of respectively n-hexane and n-heptane.

THE PROCESS CONCEPTS

For the hydroisomerization of hexane the reactor concept as shown in Figure 1 was applied.

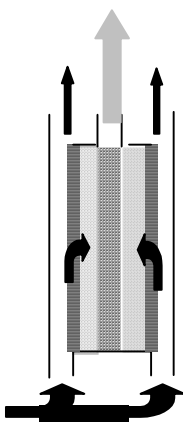


Fig. 1. Membrane reactor concept for n- C_6 hydroisomerization.

In this reactor the zeolite membrane surrounds a catalyst bed. There is no recycling of unconverted components. The process feed, mainly linear and partly branched molecules, contacts the membrane in a parallel-passage mode. The high RON branched molecules, which can be approximately 25 % of the feed, do not permeate and leave the system as a part of the

product. The linear molecules permeate through the membrane pore and are converted to equilibrium levels on the catalyst bed. The reaction products, together with the unconverted linear components, leave the system and form the remaining part of the product. Depending on the feed composition a membrane of CaA or Silicalite-1 provides the best fluxes and selectivities under the prevailing operation conditions. For the low temperature operation, i.e. 120 °C, noble metals supported on chlorinated alumina are preferred over zeolite-supported ones, since the activity of the latter is only optimal at higher temperature.

For the hydroisomerization of n-heptane we propose a concept which uses two reactors, each with a different type of catalyst, and a separation unit composed of a zeolite membrane. The first reactor contains a strong acidic bifunctional type catalyst and aims to convert sequentially n-heptane to mono- and dibranched isomers. The second reactor is used to convert mainly 2,4-dimethylpentane into 2,2,3-trimethylbutane (see Figure 4). According to the protonated cyclopropane (PCP) mechanism [2] 2,4-DMP is the main source for the formation of 2,2,3-TMB, the isomer with the highest RON (see Table 1.).

Tab. 1. Kinetic diameter and research octane number (RON) of n-hexane and n-heptane isomers

Component	Kinetic diameter (Å)	Research octane number (RON)
n-hexane (n-C ₆)	4.3	24.8
2-methylpentane (2-MP)	5.0	73.4
3-methylpentane (3-MP)	5.0	74.5
2,2-dimethylbutane (2,2-DMB)	6.2	91.8
2,3-dimethylbutane (2,3-DMB)	5.6	105.0
n-heptane (n-C ₇)	4.3	0.0
2-methylhexane (2-MHx)	5.0	42.2
3-methylhexane (3-MHx)	5.0	52.0
3-ethylpentane (3-EP)	5.0	65.0
2,3-dimethylpentane (2,3-DMP)	5.6	91.1
2,4-dimethylpentane (2,4-DMP)	5.6	83.1
2,2-dimethylpentane (2,2-DMP)	6.2	92.8
3,3-dimethylpentane (3,3-DMP)	6.2	80.8
2,2,3-trimethylbutane (2,2,3-TMB)	6.2	109.0

The catalyst used must be a moderate to weak acidic bifunctional type. Examples of catalysts used in the first and second reactor are respectively Pt/H-beta type, which can have relatively high conversion and selectivity towards isomerization and less cracking [3], and Ni supported on amorphous silica alumina [4]. The separation unit is used to separate the final product of the process composed of the dibranched 2,2-DMP, 3,3-

DMP and tribranched 2,2,3-TMB, mainly from 2,4-DMP that is send to the second reactor. A MFI type membrane with channel aperture of $\sim 5.2 \times 5.8 \text{ \AA}$ in the orthorhombic phase [5] can be applied for this kind of separation. With the kinetic diameter of 5.6 \AA for 2,4-DMP and 6.2 \AA for isomers in the product, only the smaller molecule can permeate through the channel aperture, assuming absolute separation within a perfect MFI membrane.

EXPERIMENTAL AND SIMULATION

A 10 cm silicalite-1 tubular membrane was used for the hydroisomerization of $n\text{-C}_6$. The development of this membrane is described in the paper of Gora et al. [6]. The membrane tube shown in Figure 2, consists of a porous stainless steel support, first coated with a layer of titaniumdioxide, and then a layer of silicalite-1.



Fig. 2. Silicalite-1 tubular membrane.

The membrane area comprises $2.98 \times 10^{-3} \text{ m}^2$. The reactor set-up comprised of the membrane in a hot air oven, as well as the feed and carrier gas supply units, is shown in Figure 3.

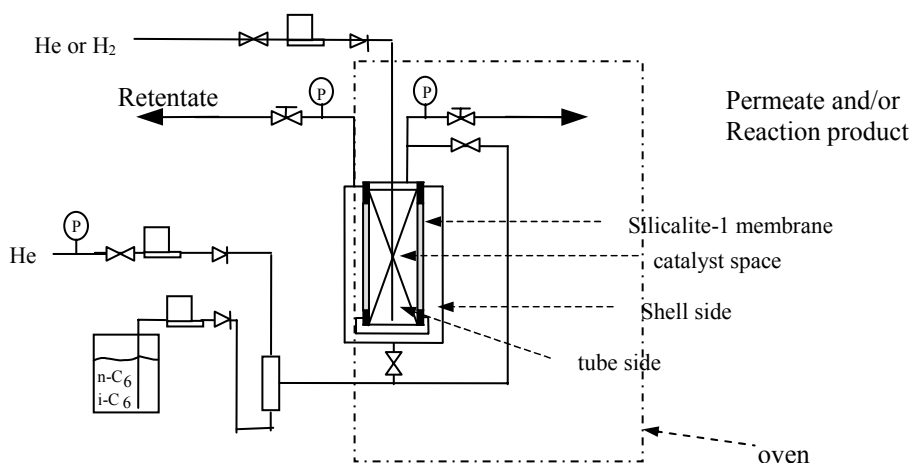


Fig. 3. Membrane reactor set-up.

Two sets of experiments were carried out to examine the performance of the catalytic membrane reactor. The first experiment was performed with no catalyst and aimed at the determination of permeation data (selectivities, fluxes) of the feed components through the membrane. In the second set of experiments the combined separation and catalytic features of the membrane reactor were analysed by filling the membrane tube (volume of $7.46 \times 10^{-6} \text{ m}^3$) with 5.39 g of platinum oxide on chlorinated alumina catalyst particles, ($7.22 \times 10^5 \text{ g catalyst/m}^3_{\text{reactor}}$) supplied by Akzo Nobel. As the feed, a mixture of 80 wt% n-C₆, 15 wt% 2-MP and 5 wt% 2,2-DMB was supplied via a HPLC pump to the system. The conditions under which the experiments were carried out are shown in Table 2. Feed, retentate and permeate streams were analysed with a gas chromatograph (FID detector for the hydrocarbons measurements). A GC-column, CP-Sil PONA CB ($50 \times 0.21 \text{ mm}$; $df = 0.5 \mu\text{m}$) was used to determine the amounts of hydrocarbons quantitatively.

Tab. 2. Operation conditions for the membrane reactor experiments

Temperature (°C)	120
Pressure tube side (bar)	4
Pressure shell side	4.5
Flow of H ₂ sweep gas (ml/min)	5
Flow of feed mixture (ml/min)	0.072
Flow of He carrier gas (ml/min)	50
Molar ratio H ₂ /C ₆ mixture	36.3
Space time ($\text{m}^3_{\text{reactor}} \text{ s/g}_{\text{feed}}$)	0.954

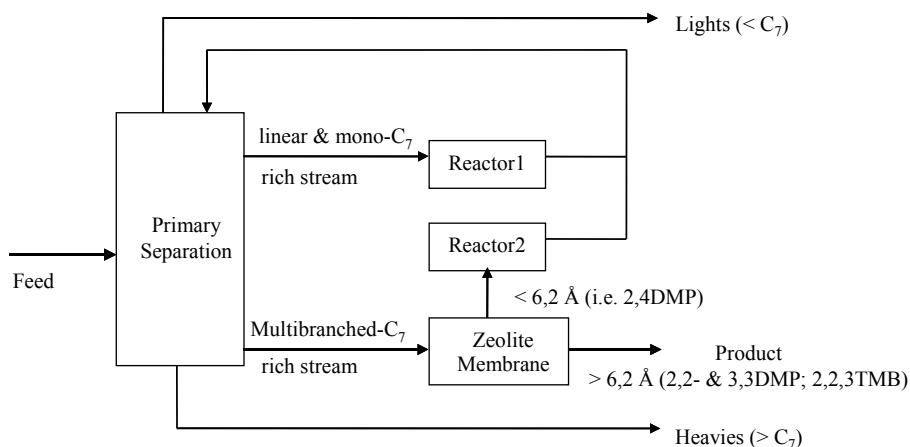


Fig. 4. n-Heptane hydroisomerization process scheme.

For the hydroisomerization of n-C₇, a process simulation was performed based on the proposed concept of two reactors and a separation unit. Figure 4 shows the process scheme. As the feed to the process, hydrogen is used as well as a simplified industrial naphtha feed with a RON of 57. The hydrocarbon feed contains C₆, C₇ and C₈ linear and isoalkanes. C₇ components comprised about 40% of the feed. The throughput of the feedstock is assumed 907 tons a day, comparable to that of the existing C₅/C₆ isomerization processes (between 600 and 1200 tons a day). The distillation train shown in Figure 4 is composed of three distillation columns. The purpose of the first two columns is to separate C₇ fraction from the heavier and lighter hydrocarbons, while the third column is used to separate the multibranched from the linear and monobranched C₇ components. The recycle stream is sent via a hydrogen separation membrane (not shown in the scheme) to the second distillation column. A detailed process flow scheme has been published recently [7].

The reactor performance estimation was based mainly on the evaluation of the reaction data of a Pt/H-beta catalyst for the first reactor [3] and of Ni supported on amorphous silica-alumina for the second reactor [4]. For hydroisomerization, a first order reaction rate was assumed. Cracking reactions were also taken into account, with mainly propane and isobutane as cracking products. These reactions were assumed to be first order in the reactant and zero order in hydrogen. Cracking was assumed to be only a function of the degree of branching:

$$k_{C, n-C7} < k_{C, MB} < k_{C, MTB}$$

k_C = cracking coefficient

The reaction models used are undoubtedly oversimplified but are nevertheless sufficient for the first approximation for the process simulation.

For the membrane performance, a simulation of a countercurrent membrane pervaporation model was used (see Figure 5.). By using this model it is assumed that the individual components do not influence each other's fluxes. The permeance data were estimated using the experimental work of Flanders et al. [8]. 2,3-DMP and 2,4-DMP were considered as the slowest permeating components and the recovery of these species was set greater than 98% at the membrane outlet.

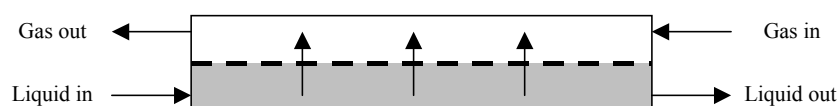


Fig. 5. Schematic view of countercurrent membrane unit.

The reactor and membrane operation conditions set for the process simulation are specified in Table 3. The process simulation was performed using Matlab and Aspen, and different membrane design configurations were calculated.

Tab. 3. Reactor and membrane specification

	Reactor 1	Reactor 2	Membrane
Reactor/membrane model	Plug flow Adiabatic	Plug flow Adiabatic	Countercurrent Plug flow
Temperature (°C)	200	300	185
Pressure (bar)	9.5	10	10 at feed side 1 at permeate side
H ₂ /Hydrocarbon ratio	8	4	-

RESULTS AND DISCUSSION

Hydroisomerisation of n-C₆

Previously it has been shown [9] that fluxes of hydrocarbons through a zeolite membrane were proportional to temperature. As opposed to the fluxes, the selectivities were inversely proportional to temperature. The optimal temperature at which selectivities and fluxes were good, and the catalyst was expected to be still active was 120°C. In the separation of a mixture at relatively low temperature, for the molecules that fit into pores, competitive adsorption of components governs the separation selectivities. n-Hexane as the strongest adsorbing species, effectively blocks pores for other mixture components. With increasing temperature, adsorption becomes less dominant and the intrinsic diffusivity of molecules inside the zeolite starts to play a role. At the optimum temperature of 120°C, fluxes (Φ) of the feed components through the membrane as well as the separation selectivities (α) were calculated from the experiments without the presence of a catalyst (see Table 4.). These results show that the n-C₆ flux and the selectivities are sufficiently high, indicating a relatively good membrane performance.

Tab. 4. Flux (Φ_i) and separation selectivity (α) of the different components

i component	Φ_i (mmol/m ² s)	$\alpha_{i(2-MP)}$	$\alpha_{i(2,2DMP)}$
n-C ₆	$3.04 \cdot 10^{-2}$	11.78	15.28
2-MP	$5.25 \cdot 10^{-4}$	-	1.30
2,2-DMB	$1.48 \cdot 10^{-4}$	-	-

The composition of the feed, permeate (experiment with no reaction) and product stream (experiment with reaction) as well as the reaction product distribution at thermodynamic equilibrium and the product selectivities are given in Table 5. It is clear that the catalyst used is active in the hydroisomerization reaction of n-hexane at 120°C. For the isomers 2-MP and 2,3-DMB a combined product distribution value was given, as the GC-column could not be optimised to separate perfectly these two components. At the condition set for hydroisomerization, a n-C₆ conversion of 86.5% was achieved. The table also shows that the isomerised product is near the thermodynamic equilibrium, which indicates the high activity of the catalyst. As it can be seen from Table 5 the reaction is very selective towards isomerization compared to cracking, since less than 3% of the converted n-hexane is cracked into smaller components. The high selectivity towards the dibranched component 2,2-DMB, besides 2,3-DMB, is of great importance when aiming at larger RON. The estimated reaction product RON (excluding n-C₆) is 85.

Tab. 5. Distribution of hexane isomers and product selectivities at T = 120 °C, Δp = 0.5 bar

i component	Distribution (%)				S _i (%)
	Feed	Permeate	Reaction product	Equilibrium	
n-C ₆	80	97.83	12.96	7.72	-
3-MP	-	-	13.29	15.00	15.65
2-MP	15	1.69	36.75*	37.28*	41.31*
2,3-DMB	-	-			
2,2-DMB	5	0.48	34.60	40.00	40.21
Cracked (<C ₆)	-	-	2.40	-	2.83

* 2-MP + 2,3-DMB

Hydroisomerisation of n-C₇

The total process simulation with 907 tons a day of feedstock resulted in 220 tons a day of product with RON of 92 containing mainly 2,2,3-TMB, 2,2-DMP and 3,3-DMP with a weight composition of 19, 46 and 34% respectively. The amount of product compared to the feed is rather low, about 24%, because of the initial separation of C₆ and C₈ components. However, there was a RON upgrading of 35 points from feed to the product, which is approx. 25 points more than the conventional C₅/C₆ processes.

Membrane design considerations

For the separation of the isomers a membrane area of 2×10^5 m² was calculated. Assuming a ten times faster permeability, because of a ten times smaller membrane thickness than that used in [8], the required membrane area will be reduced to 2×10^4 m², which is a reasonable area to use in a design. Hexane isomers permeation data were obtained from [8]. The

extension of these data to heptane isomers is not totally correct, but nevertheless it can give a reasonable estimation of the total membrane area based on the assumption of the permeance for hexane and heptane being of equal order of magnitude. Permeance data on branched heptane isomers is scarce. For the calculation of the dimensions of the membrane unit different geometries can be used as applied in membrane technology for industrial application. The most straightforward solution is the shell and tube configuration (Figure 6a).

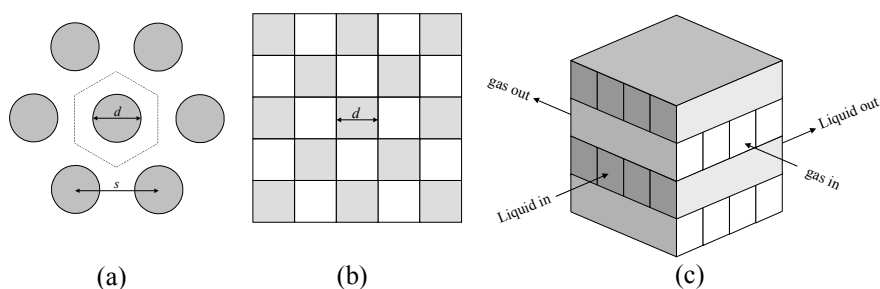


Fig. 6. Different membrane geometries: (a) Shell and tube membrane unit (top view); (b) Countercurrent monolith (top view); (c) Cross-flow monolith.

It is similar to a countercurrent heat exchanger but here mass is exchanged. One of the disadvantages is the large internal volume of the unit (low membrane surface to the unit volume ratio). Monolith structures, however, have a very high surface to the volume ratio. They consist of a large number of parallel square channels with sizes ranging from 10 to 100 cells per square inch (CPSI). Although in theory these structures can be applied in the countercurrent mode (Figure 6b), it will be practically impossible to connect all individual channels to the corresponding process streams. A feasible solution is the cross-flow monolith [10, 11] shown in Figure 6c. In this structure cross flow can be established because each layer of channels is rotated by 90° . By interconnecting multiple units one can approach countercurrent operation.

The results of the calculations of unit dimensions of the different options are given in Table 6. To decide which configuration should be used, one must make a choice in the limiting factor: the fluid velocities or minimal dimensions of membrane units. The dimensions given in the table are not currently produced commercially for a large MFI-type zeolite membrane unit. Thus, the technical feasibility of the process is restricted by commercial development of MFI-type zeolite membranes on the industrial scale.

Tab. 6. Unit dimensions for two membrane unit options

	Shell and Tube system	Cross-flow monolith
Membrane area	20000 m ²	20000 m ²
Channel size	25 mm (tube I.D.)	2.5 mm (100 CPSI)
No. of units	4	1
No. of channels per unit	6366 tubes	2×10 ⁶ channels
Unit volume	62 m ³	50 m ³
Unit dimensions (L×D or L×W×H)	10×2.8 m	4×4×3.1 m
Liquid velocity	0.7 mm/s	1.5 mm/s
Gas velocity	1.0 m/s	2.2 m/s

To evaluate the cost of the process simple measurements of cost estimation were used [12]. The purchase cost of equipment is estimated in 9.5 million €, which is relatively higher than conventional state of the art processes. The cost distribution is shown in Figure 7. The main cost driver as can be seen from Figure 7 is the membrane, showing that the economic viability of the process strongly depends on the membrane price. The price per m² of the membrane was based on currently commercialised zeolite A type membranes [13].

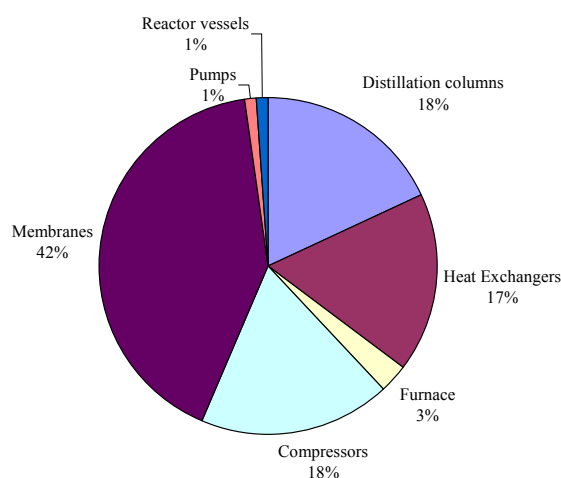


Fig. 7. Equipment cost distribution.

CONCLUSIONS

The results of the n-hexane hydroisomerization experiments performed in the integrated membrane reactor composed of silicalite-1 and Pt supported on chlorinated alumina catalyst strongly indicates the technical feasibility of this process within a membrane reactor concept. This concept gives high selectivities as well as high RON compared to the state of the art

processes. The heptane hydroisomerization process simulation based on the two reactors and a zeolite membrane concept indicates interesting features on industrial scale from the octane enhancement point of view. Starting from a 907 ton a day of feed a 220 ton a day of product with RON of 92 is obtained. The product yield is low, however, there is an improvement in the research octane number from 57 up to 92, which is higher than conventional hydroisomerization processes. The further technical and economical development of these processes strongly depends on the progress of industrial scale MFI-type zeolite membrane.

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