

layer can become incorporated or excluded by the lyospheres at the surface of the latex particles. Thus, the stability of the disperse systems can dramatically change.

- Conformational changes in the lyospheres can be determined by microcalorimetric measurements. Enthalpy and entropy effects in the adsorption layer and in the bulk liquid as well and the swelling processes of the colloidal particles were verified. Thus, it is possible to analyze the displacement of one component of the binary liquid system by the other with microcalorimetric measurements.

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# Membrane Coalescence for Phase Separation of Oil-in-Water Emulsions Stabilized by Surfactants and Dispersed into Smallest Droplets

By Sandra Hoffmann and Walter Nitsch\*

## 1 Introduction

In the field of chemical engineering separation processes, such as extraction or distillation of heteroazeotropes, severe problems in phase separation of oil/water (o/w) dispersions containing very small droplets exist [1]. This is especially true if the bulk phases contain surfactants stabilizing the interface and thus inhibit coalescence, a situation which often occurs in technical applications. Yet in this particular case, mechanical separation apparatus come to their operational limits since the conventional coalescing aids, such as plate separators or fiber beds, separate mainly in the droplet diameter range closely beneath 100  $\mu\text{m}$  and in the absence of surfactants [2–5].

On the other hand, rapid coalescence can indeed be observed for an o/w emulsion, even a highly stable one with oil droplets down to 1  $\mu\text{m}$ , after being pumped through a hydrophobic, microporous membrane [6,7]. Thus, recent studies presented in [8] have explored phase separation due to “membrane coalescence” for various emulsions stabilized by surfactants while aiming to investigate the performance as well as the operational limitations. Another aspect was to characterize the process with regard to plausible elementary steps in the physical mechanism.

## 2 Experimental

The process principle is defined by three functional segments of the pilot plant (Fig. 1), the membrane coalescence (II) as central unit, the preparation of o/w emulsion feed (I), as well as the phase separation unit (III) at the end.

### 2.1 Preparation of a Stable O/W Emulsion

First, a test emulsion (if untreated stable for weeks) is prepared by dispersing (recirculating about 20 times for a 50 l batch), either by gear pump (‘M 838’, Schwinherr, flux 150 l/h) or – in the case of high-viscosity oil phases – according to the rotor-stator method (in-line dispersing tool ‘IKA-Super-Dispax SD 41’). The droplet diameter distributions of the emulsions were analyzed by measuring diffraction (‘LS 230’, Coulter Electronics, including ‘Polarization Intensity Differential Scattering’). To attain a good comparability, the test

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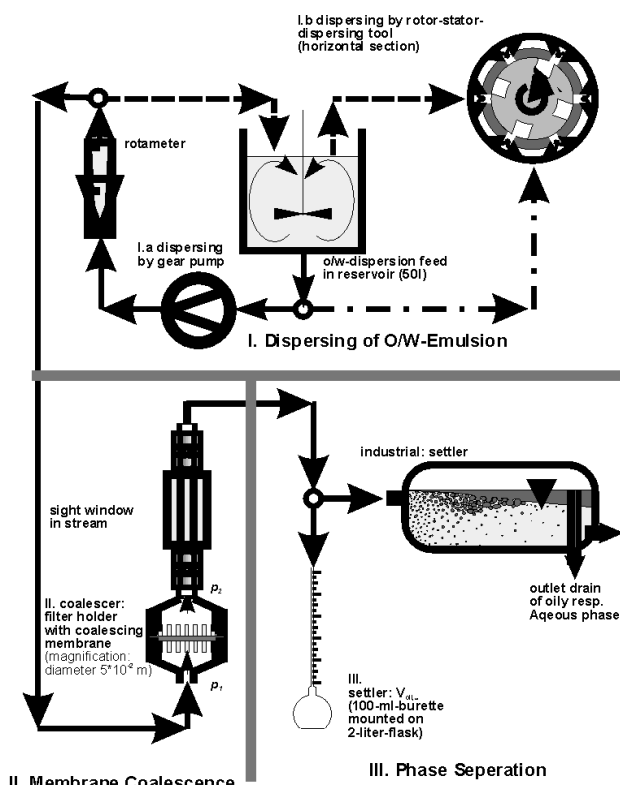


Figure 1. Scheme of experimental plant.

emulsions were dispersed in such a way that equal droplet sizes could be achieved, i.e., in the range of ca. 1 to 10  $\mu\text{m}$  (Sauter diameter  $d_{1,2} \cong 4 \mu\text{m}$ ). Process development was mainly carried out with technical-grade isododecane/water as a model effluent, thus always with 0.1 molar additive of DEPA [bis(2-ethyl-hexyl)-phosphoric acid] as a typical interfacially active complexing agent (thus  $\lambda = 22 \text{ e-3 N/m}$ , compared to  $\lambda = 46 \text{ e-3 N/m}$  for pure water/isododecane). The effect of the dispersed phase was investigated by the respective variation of the o/w concentration ( $c_0 = 0.1$  to 7 vol.-%) and of the dynamic viscosity ( $\eta_d = 1.0$  to 106 e-3 Pa s) with aliphatic components (paraffins/DEPA). A separate study was carried out on the influence of surfactants by employing diverse nonionic ones (row of homologous  $\text{C}_{16}\text{EO}_x$ ; Brij 52/56/58) representing a class with a broad application field.

## 2.2. Plant Unit of Membrane Coalescence

Center part is the coalescer, a hydrophobic, microporous, very thin (0.11 mm) membrane ( $\text{Ø} 50 \text{ mm}$ ) in a filter holder, through which the prepared stable test emulsion is transferred by a gear pump (flux up to 190 l/h). Usually the membrane lies in-between two polypropylene frits of a polycarbonate filter holder ('SM 165 08 B', Sartorius). The coalescing membrane serving us as a standard (Sartorius '11842') shows a stretched, sponge-like pore structure featured by a high porosity of 69 % and an average diameter of 5  $\mu\text{m}$ .

Immediately subsequent to the filter holder the coalesced phases stream through an observation window also for purposes of photographical characterization. In order to enable a direct view onto the membrane itself while in function and onto the outlet dispersion passing at a low flow rate, a special clamping device combining an observation window and a filter holder was furthermore developed [8].

In order to study the physical course of wetting and coalescing inside the membrane, the organic load  $v_{org, M}$  held up inside the membrane pores under stationary flow conditions was experimentally determined and standardized with the free membrane pore volume. After extraction of the complete membrane contents (isopropanol), the volumetric fraction of organic load can be detected by UV/VIS spectrometry, if the aliphatic main phase had been doted by a small portion of toluene beforehand (13 vol.-%).

## 2.3 Determination of Phase Separation Efficiency

After passage through the coalescer, the dispersion which, having taken a glance through the observation window, appears to have a significantly enlarged diameter spectrum [8], is led to a settler, or alternatively into scaled settling flasks which serve to determine volumetrically the phase separation efficiency  $\eta$  commonly defined by<sup>1)</sup>:

$$\eta = \frac{V_{org, \omega}}{V_{org, \alpha}} \cdot 100 [\%]$$

## 3 Results and Discussion

### 3.1 Phase Separation for Alkanes with 0.1 Molar Add of DEPA

The performance of the membrane coalescence can be derived from the separation efficiencies reached (standard emulsion) and their dependence on the flow rate (Fig. 2).

In a range of oil-in-water concentrations between  $c_0 = 0.3$  and 7 vol.-% for the standard emulsion and in a range of flow rates from  $J_{min} = 25 \text{ m}^3/\text{m}^2\text{h}$  up to about  $650 \text{ m}^3/\text{m}^2\text{h}$  constant and high separation efficiencies of 95 % can be reached, whereby the upper limitation is produced by the available pump power with a cross-sectional membrane area  $A$  of 2  $\text{cm}^2$  (reduced by a circular diaphragm). The experimental results in regard to separation efficiency  $\eta$  for an organic fraction as low as  $c_0 = 0.1$  vol.-% seem to mark the beginning of a performance limit for highly diluted emulsions.

In addition to that, another variable seems to be a very relevant one for the standard experiment ( $[\text{DEPA}] = 0.1 \text{ M}$ ;  $c_0 = 3.3$  vol.-% oil; droplet diameter  $d_{1,2} \cong 4 \mu\text{m}$ ), i.e., the viscosity  $\eta_d$  of the organic dispersed phase.

1) List of symbols at the end of the paper.

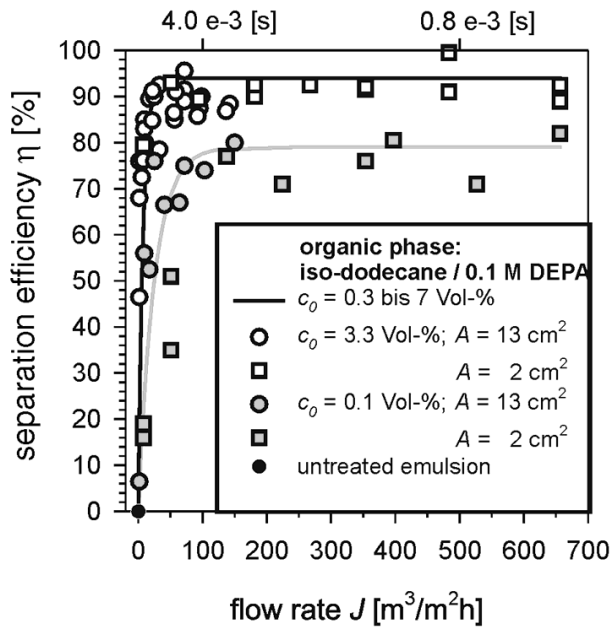


Figure 2. Effect of flow rate  $J$  and of O/W concentration  $c_0$  of emulsion (two exemplary residence times  $\tau$  on upper abscissa).

From Fig. 3 showing the dependence of separation efficiency  $\eta(w)$  it can be seen that unchanged high values of about 95 % can be reached for emulsions with an oil viscosity of two dimensions higher as compared to iso-dodecane ( $\eta_d = 1.0e-3 \text{ Pa}\cdot\text{s}$ ). Yet, the technically interesting range of flow rates connected to maximum separation efficiencies becomes shorter with an increase of oil viscosity. Thus, for the separation of viscid oil phases, still with high flow rates correspondingly large membrane areas must be applied.

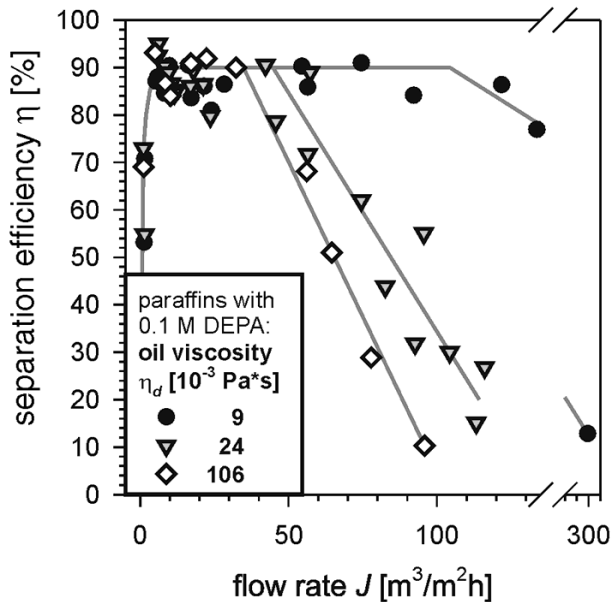


Figure 3. Effect of oil viscosity  $\eta_d$  on flow rate dependence on separation efficiency  $\eta(J)$ .

### 3.2 Phenomenology of Coalescence

For the experimental characterization of membrane coalescence two quantitative features can serve as key indicators:

- the stationary organic load inside the membrane pore volume stationarily permeated by the two emulsion phases and
- the volume fraction of the dispersed phase which can be photographically determined in the observation window at the membrane outlet.

In regard to the “oily holdup” it can be stated that the fraction of the oil phase inside the stationarily permeated membrane  $v_{org, M}$  is about ten times higher than in the membrane inlet emulsion stream  $c_0$  (Fig. 4: aggregation factor  $f \cong 10$  up to 15 in the flow-independent plateau range up to  $J_{min} = 25 \text{ m}^3/\text{m}^2\text{h}$ ). Thus, we observe aggregation of organic load inside the membrane only merely dependent on the o/w concentration  $c_0$ , a situation which can only be interpreted as caused by wetting of the hydrophobic membrane.

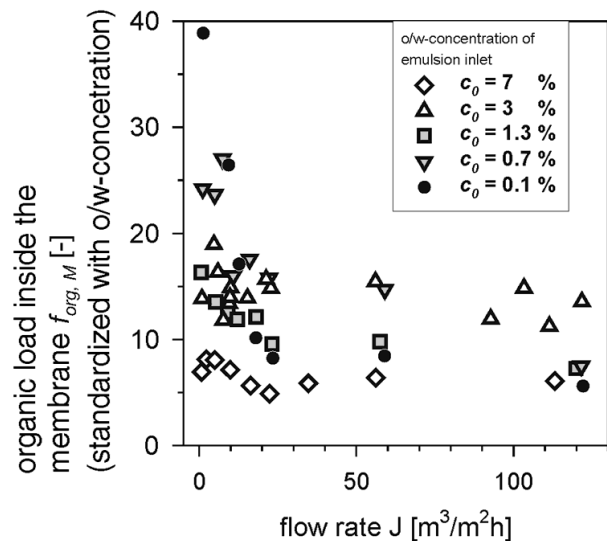


Figure 4. Effect of flow rate on standardized organic load inside the membrane  $f_{org, M}$  for various O/W concentrations  $c_0$  (isododecane/0,1 M DEPA).

A fact more puzzling at first impression concerns the fraction of dispersed phase which can be detected in the membrane outlet zone (for details see [8]). Plainly derived from the portion of area fill, this fraction is about 60 % for the standard emulsion containing  $c_0 = 3 \text{ vol.-%}$ . This leads to the conclusion that these dispersed particles of several millimeters in size cannot be considered as coalesced oil phase but as oily domains carrying huge amounts of enclosed water. The said particles are instable, i.e., they will immediately coalesce inside a settler. Such ‘liquid/liquid-foam structures’, leaving the uncovered membrane surface, can be directly observed viewing the membrane freely clamped by a special device as mentioned above and permeated at low flow velocity [8].

The process of coalescence caused by the in-line-passage of a membrane must also be related to the features of the permeated pore system. On the one hand, coalescence of

dispersed oil droplets will only occur in the case of hydrophobic surfaces (PTFE, PP, no effect for hydrophilic cellulose acetate). On the other hand, one can note that the membrane pore size will also be a determining factor. Since there is experimental proof that with pores of middle size of  $d_{pore} = 0.22$  resp.  $1.0 \mu\text{m}$  no coalescence can be achieved for a droplet size range at about  $5 \mu\text{m}$  whereby pore sizes of  $d_{pore} = 3, 5$  resp.  $10 \mu\text{m}$  yield very decent separation efficiency (membranes of Millipore). Therefore, there appears to be an obvious correlation between particle and pore size, so that droplet coalescence requires a sufficiently wide pore system.

### 3.3 Effect of Substance Matter on Phase Separation

For the derived principle for breaking of emulsions stabilized by surfactants, the influence of the substance matter ought to be considered as well, especially in regard to enabling preevaluation of the technical feasibility. Thus, nonionic surfactants, "Brij"-homologues, were tested and varied in concentration in order to be characterized by their separation efficiency.

For the lipophilic Brij 52 ( $\text{HLB} < 10$ ) a behavior corresponding to DEPA was observed, whereby still a decrease of separation efficiency was noted falling from 90 % for  $c_T = 10 \text{ mg/l}$  isododecane down to 70 % for  $c_T = 1000 \text{ mg/l}$  (surface tensions at  $\gamma = 20$  resp.  $2 \times 10^{-3} \text{ N/m}$ ).

Phase separation occurred much more dependant on the concentration (Fig. 5) in the case of hydrophilic Brij 56 ( $\text{HLB} > 10$ ). Then, also high separation efficiencies are

generated at high throughputs, however, limited only by concentrations up to  $c_T = 10 \text{ mg/l}$  water. With the further increase of concentration up to  $100 \text{ mg/l}$  and more, the maximum separation efficiencies severely drop down to 30 %, an effect which goes along with intensifying restraint in attainable throughputs.

Concerning the experiments on the effect of the surfactant concentration of Brij 56 (as well as Brij 58) on the separation efficiency, the following remarkable point was observed: a comparably mediocre phase separation, caused by the inhibition of coalescence at the principle phase interface in the settling flask; yet at the same time an occurring inversion of dispersion from water-in-oil domains (in continuous aqueous phase, i.e., a three-phase system) to an oil-in-water dispersion (two phases) (for details see [8]).

Within hours this o/w dispersion, through drainage of the continuous aqueous phase, increases in oil concentration so that phase separation can be easily completed by mere centrifugation of this minor o/w dispersion fraction (concentrated up to ca. 80 % oily phase compared to 3 vol.-% in the initial emulsion).

This first experimental screening in relation to assorted surfactants and at various concentrations makes it obvious that for an advanced comprehension of optimal separation conditions supplementary aspects of colloidal chemistry as to dispersion stability have to be considered. Only with this perception, the regular conditions for the technical feasibility of a membrane coalescence process will be completely definable.

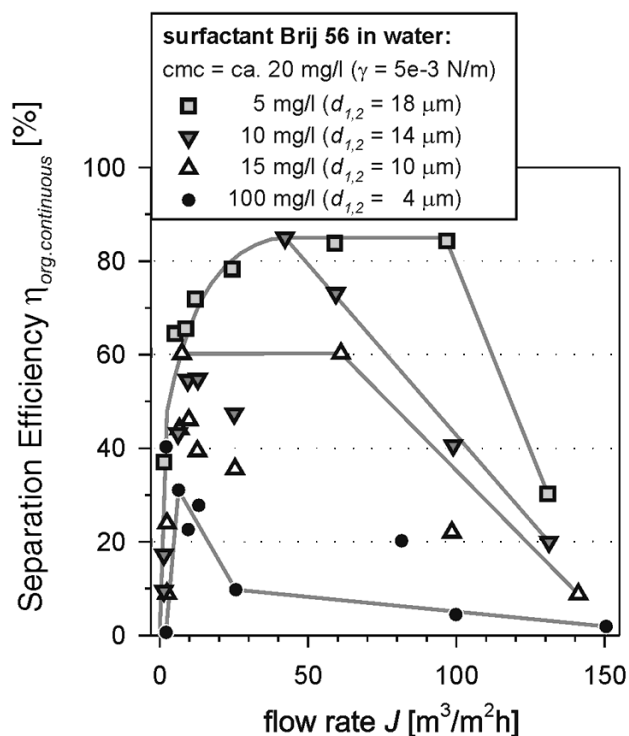


Figure 5. Separation efficiency  $\eta_{org,c}$  in the presence of hydrophilic surfactant Brij 56.

### 3.4 On the Physical Mechanism of Membrane Coalescence

A physical model mechanism of the "membrane coalescence" [8] is supposed to give a plausible interpretation especially as to the relevant observations. Thus, explicable ought to be the following key conclusions: the oily holdup inside the membrane pore structure, the particle aggregation of emulsified oil droplets, the occlusion of water in oil, the emergence of macroscopic w/o domains as well as the effect of the pore size.

Local parameters determining for membrane coalescence unfortunately cannot be investigated; this is due to the small membrane thickness (0.11 mm) itself and, at concurrently high superficial velocities, also due to very short residence times in the range of milliseconds. Therefore, modeling must be limited to qualitative characterization and mechanisms. Thus, the porous membrane will be approximated as capillaries connected with one another, so that in regard to the geometry the flow of emulsion through a singular capillary can be considered as characteristic in first estimation.

Our suggestion for a plausible mechanistic course can be conceived from the displayed scheme of Fig. 6. First, wetting of emulsified oil droplets occurs on the hydrophobic capillary walls. Second, aggregation takes place due to particle

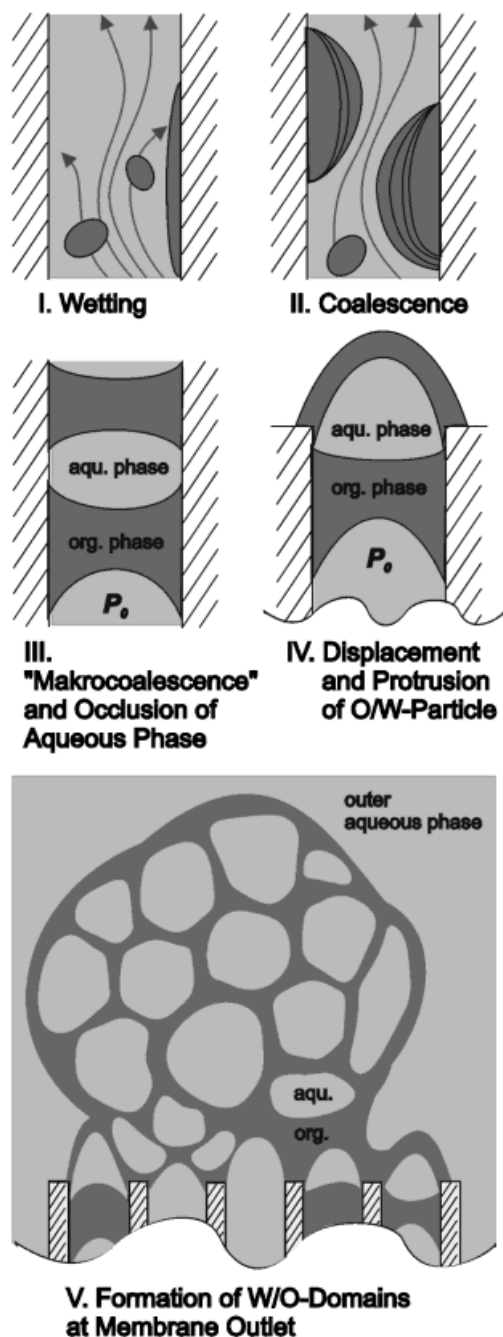


Figure 6. Initial phase. Holding up stationary oily load – conditions for aggregation.

coalescence with already wetted spots, an effect to be considered as mainly responsible for the oily holdup. As a third step, water occlusion in oily phase will be caused, since along the axis several diametrically located oily domains start to coalesce. Thus, step IV, the existing dynamic pressure yields the driving force for the formation of water-in-oil droplets at the pore outlet.

Taking the reality of a net pore structure into account by a model of many parallel capillaries connected to one another, the formation of observed enormous water-in-oil domains

becomes conceivable; this is supposed to be due to the oil wetting of the exterior membrane surface by which the singular procedures lead to the observed collective one as the emergence of huge w/o domains.

Since it is also clear that this scheme is bound to the condition  $d_{pore} \geq d_{1,2}$  the empirical absence of coalescence for  $d_{pore} \ll d_{1,2}$  can be understood.

#### 4 Membrane Coalescence as a Technical Process

While a general feasibility of the novel process, especially for emulsions stabilized with multiple and diverse surfactants, cannot yet be claimed, the perspectives of the membrane coalescence as a high potential application can still be shown by comparison to the state-of-the-art fiber bed coalescer. From Tab. 1 one can derive the range of high throughputs (in combination with relatively low pressure drops [8]), an obviously high flexibility in relation to organic droplet size and volume fraction of the o/w emulsion as well as the revealed conceptual possibility of breaking long-term stable emulsions.

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Table 1. Membrane versus conventional fiber bed.

Surfactant	Membrane Coalescence [8]		Fiber Bed Coalescer [9] [4,5]	
	yes	no	partial	no
O/W concentration [vol.-%]	0.1–7		2–5	0.1–0.2
Droplet- $\varnothing$ at inlet [ $\mu\text{m}$ ]	1–10		< 100	10–100
Flow rate $J$ [ $\text{m}^3/\text{m}^2\text{h}$ ]	3–660		2.5–65	7–47
Separation efficiency $\eta$ [%]	ca. 80–98		complete/partial	50–98

#### Symbols used

$A$	[ $\text{m}^2$ ]	active membrane area
$c_0$	[vol.-%]	o/w concentration of the test emulsion to be separated
$c_T$	[g/l]	concentration of surfactant
$d_{1,2}$	[ $\mu\text{m}$ ]	Sauter diameter of droplet size distribution
$d_{Pore}$	[ $\mu\text{m}$ ]	nominal pore diameter of the membrane
$f$	[1]	aggregation factor (organic load in membrane standardized with $c_0$ )
$\gamma$	[ $10^{-3}\text{N/m}$ ]	surface tension
$\eta$	[%]	separation efficiency
$\eta_d$	[ $10^{-3}\text{Pas}$ ]	dynamic viscosity of the organic dispersed phase
$J$	[ $\text{m}^3/\text{m}^2\text{h}$ ]	area specific throughput (flow rate)
$\tau$	[s]	mean residence time inside the membrane
$V_{org, \alpha}$	[l]	initial volume of the organic phase

$V_{org, \omega}$  [l] separated volume of the organic phase  
 $v_{org, M}$  [vol.-%] fraction of organic load inside the free membrane pore volume

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# Diesel Oil from Natural Gas by Fischer-Tropsch Synthesis Using Nitrogen-Rich Syngas\*

By Andreas Jess, Kurt Hedden, and Rüdiger Popp\*\*

## 1 Introduction

### 1.1 Background

About 50 % of the proven natural gas reserves are today distant from any sizable market, e.g., large reserves in the Middle East. The economic utilization of this natural gas is limited by its costly transportation. This also applies to small

gas fields and to oil-associated gas, because flaring will be charged with taxes.

An option to bring remote natural gas to market is its conversion by Fischer-Tropsch synthesis (F-T. synthesis) into higher hydrocarbons, like liquefied petroleum gases, gasoline, diesel oil and wax. Especially the last two products are of high value: Diesel oil with a cetane number of more than 70 is of very good quality and is free of sulfur or other impurities. Wax is an excellent feed for hydrocracking to produce additional amounts of diesel oil. Gasoline with a poor octane number of about zero has to be improved by further chemical conversion. It is therefore desirable for the F-T. synthesis to produce as much long-chain hydrocarbons as possible.

The products of F-T. synthesis can be easily shipped obviating the need for dedicated cryogenetic transportation, equipment and tankage. Therefore, in recent years, a world wide “renaissance” of the F-T. synthesis can be stated, and several processes for the conversion of natural gas into liquid fuels have been investigated and tested in pilot plants (e.g., EXXON, SHELL, SASOL, TEXACO/ARCO/SYNTROLEUM [1–4]; overview in [5]). The majority of these processes are based on nitrogen-free (or very lean) syngas produced from natural gas either by partial oxidation with oxygen or by steam reforming (or by a combination of both). The syngas is then subsequently converted by F-T. synthesis in multitubular fixed-bed reactors, slurry reactors or circulating fluidized-bed reactors. The production costs of these processes are probably still above the break-even point, at least at the oil price of today (end of 1999).

### 1.2 New Concept for Diesel Oil Production from Natural Gas

Common concepts for the production of higher hydrocarbons from natural gas are based on the assumption that the efficiency in terms of kg liquid fuels per m<sup>3</sup> of natural gas should be as high as possible in order to keep energy and feedstock costs down; investment costs therefore are high. For countries in remote areas with low prices of energy and natural gas, respectively, an *economic* solution is probably a *low-cost technology* even if the conversion efficiency is lower [6].

An interesting alternative to common capital-intensive processes therefore is the concept shown in Fig. 1. After desulfurization, natural gas is converted at a total pressure of 25 bar into a nitrogen-rich (about 50 vol.-% nitrogen) and soot-free syngas by Ni-catalyzed partial oxidation *with air*. Using air instead of oxygen eliminates the need of a costly air separation plant. Only an air compressor is needed, as natural gas is normally available at a higher pressure. Without further compression the nitrogen-rich syngas is converted by F-T. synthesis in multitubular fixed-bed reactors into higher hydrocarbons. The proposed process with nitrogen-rich syngas does not utilize a recycle loop to avoid any build-up of nitrogen in the system. This configuration is probably less expensive because a recycle compressor is not needed. The dilution of the syngas with nitrogen plays a significant role by

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