

Tar Removal from Gasification/Pyrolysis by Emulsion Liquid Membrane: A Short Overview

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Adhi Kusumastuti¹, Samsudin Anis^{1,*}, Nur Qudus¹, Widi Astuti¹

¹ Faculty of Engineering Universitas Negeri Semarang, Kampus UNNES Sekaran, Gunungpati, 50229 Semarang, Indonesia

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ABSTRACT

Tar is among undesirable by-products of producer gas generated from gasification/pyrolysis of biomass. Due to the erosive and corrosive characteristics of tar, a number of tar removal studies have been done. However, considering tar availability in deficient concentration, a highly selective and energy economics method is of importance. Emulsion liquid membrane is a choice of selective and economics method. Some studies on tar removal using emulsion liquid membrane were reported. Information about definition and transport mechanism of emulsion liquid membrane was given. Effects of emulsion formulation on tar removal were described. Effects of some operating conditions in permeation process on tar removal were also presented. The study found that types and concentration of surfactant and diluent as well as emulsification methods need to be properly considered for better result. Whereas permeation speed, volume ratio, and equipment used greatly affect the emulsion breaking and tar removal efficiency. Considering low emulsion breaking, application of Taylor-Couette column as the permeation equipment for further tar removal study is proposed.

Keywords:

Emulsion liquid membrane; tar removal;
Taylor-Couette column

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1. Introduction

Among the world current issues are the emissions of CO₂ that trigger global climate change. This major issue has encouraged many researchers to find greener sources of energy as alternatives to fossil fuels. It is therefore investigations on renewable energy sources have become inevitable. Biomass is a source of renewable energy sources. Regardless being the promising biomass utilisation method, some by-products like fly ash, NO_x, SO₂, and tar are also generated by gasification process despite the main products, i.e., fuel gases, char, and chemicals. The by-products are harmful since they can lead to erosion and corrosion on metals. Previous study of Belgiorino *et al.*, [1] found that tar is among the contaminants present in producer gas. Study of Yusoff *et al.*, [2] revealed that the

* Corresponding author.

E-mail address: samsudin_anis@mail.unnes.ac.id

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highest liquid smoke proportion of 36.93 wt% was generated from pyrolysis of coconut shell at reaction temperature of 220°C.

The above description indicates that despite the benefits in replacing fossil fuel, producer gas from biomass gasification also potential in generating undesirable by-products. Many researchers have paid attention to removing tar as a contaminant in the producer gas. A significant number of tar removal studies have been reported to date. The tar content in producer gas depends on gasifier types. For example, an air-blown circulating fluidised bed biomass gasifier contains about 10 g/m³ tar. In general, tar content varied in the range of 0.5 to 100 g/m³ [3]. Being the major problem in the employment of producer gas in downstream applications, tar removal has not entirely been settled. Before employed in gas turbines and internal combustion engines by turbocharger, producer gas needs to be compressed. So does the air, in case of the operating condition of gasifier is at atmospheric pressure. Saturation occurs when tar vapour pressure beyond tar saturation pressure, thus results in the condensation of saturated vapour. It generates the blocking of downstream pipelines, which in turn foul engines and turbines. Tar is classified into four product classes, i.e. (1) primary products, consist of cellulose-derived, hemicellulose-derived and lignin-derived products; (2) secondary products consist of phenolics and olefins; (3) alkyl tertiary products consist of methyl derivatives of aromatic compounds; and (4) condensed tertiary products consist of PAH series without substituent [4]. Based on the components, i.e., chemical, solubility and condensability of different tar compounds, and rather than reactivity of the compounds, tar is classified into five classes, i.e., GC-undetectable, Heterocyclic, Light aromatic (1 ring), Light PAH compounds (2–3 rings), and Heavy PAH compounds (4–7 rings). The successful application of producer gas of which is determined by selectivity performance of tar treatment of class 2, 4, and 5 tar, either by tar removal or tar conversion. Among class 2 tar is pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol. Based on the tar removal location, the methods are categorised in two types, i.e., primary method (tar removal in the gasifier) and secondary method (tar removal outside the gasifier).

Tar treatment from producer gas should be carried out through secondary method using wet and hot gas treatment. Despite the ideal stages in the gasifier (primary method), a satisfactory solution has not been achieved yet. Many low tar emissions were found in some primary measures; however, few problems came from feedstock availability and scale-up, generation of waste streams, reduction of cold gas efficiency, construction of complex gasifiers, and narrow operating windows [4]. Significant decrease of tar content treated using primary method; however, secondary method is inevitable to reach complete removal. Tar removal is very possible to be done using secondary method as a single method without the application of primary method. Utilisation of water in tar removal from gas remains another environmental problem, since the used water would be contaminated with harmful chemicals such as phenol. A follow-up process should be carried out to recover phenol from wastewater.

Low tar concentration but harmful effects on environmental and human being needs selective and economical removal method. Emulsion liquid membrane is a solution of selective and economical method for removing tar. Despite the establishment of emulsion liquid membrane, emulsion instability is still a significant problem. Emulsion formulation and emulsification methods have been widely investigated to produce stable emulsion, thus provide better extraction efficiency. The conventional stirring method for extraction process is another disadvantage of this method. Higher stirring rate offers better extraction efficiency but may be harmful to emulsion stability. Application of Taylor-Couette column for emulsion liquid membrane is believed to be able to remove solute at high efficiency and shorter time [5].

Some studies on tar removal using emulsion liquid membrane (ELM) have been done. Dong *et al.*, [6] investigated simultaneous removal of tar and dust by emulsion liquid membrane method. They

found that under-investigated operating conditions, tar and dust removal efficiencies were 98.32% and 96.37%, respectively. Another study on tar removal was done by Zhang *et al.*, [7]. They developed emulsion liquid membrane method to remove tar from coke oven flue gas. Parameters including concentration of surfactant, gas flow rate, separation, and emulsion stirring speed and volume ratio of oil phase to internal phase were studied. Removal efficiency of tar from coke oven flue gas of about 98 % was obtained at optimal operating conditions. Habaki *et al.*, [8] examined batch permeations of coal tar absorption oil using employing stirring vessel as a contactor. They studied the effects of selected additives on emulsion liquid membrane permeation. It was found that nitrogen heterocyclic compounds were selectively permeated under emulsion liquid membrane system. Applications of methanol and di-ethylene glycol were more effective in enhancing the permeation rates of the components. Overall volumetric permeation coefficients approximately increased with the distribution coefficients. Separation of coal tar absorption oil by emulsion liquid membranes was done by Shimada *et al.*, [9]. Mass transfer rate of absorption oil separation was examined under emulsion liquid membrane. Some organic phases and water were employed; the liquid-liquid equilibrium of components contained in absorption oil was measured. They revealed that distribution coefficients of nitrogen heterocyclic compounds were always larger than those of homo cyclic compounds. Distribution coefficients of system using heptane in organic phase were higher than those of toluene with higher polarity. Nitrogen heterocyclic compounds could selectively permeate and be separated from other hydrocarbon compounds. Effects of mass transfers by membrane breakage and entrainment on permeation rate were negligible. Putrawan *et al.*, [10] applied emulsion liquid membrane process for recovering dimethyl naphthalene from light cycle oil. They simulated the recovery of dimethyl naphthalene from light cycle oil. Transfer of hydrocarbon under oil in water in oil emulsion liquid membrane system was investigated [11]. Simulation was developed by dimensionless multi-layer liquid membrane model to improve separation selectivity of emulsion liquid membrane system. They suggested the decrease in the number of inner oil droplets in emulsion drop to increase the selectivity.

The purpose of this work is to present a short overview of recent studies on the application of emulsion liquid membrane technology to remove tar generated from thermochemical processes of materials. Emulsion formulation and permeation process affect tar removal efficiency thus highlighted to get a new insight about better emulsion liquid membrane conditions for clean producer gas production.

2. Emulsion Liquid Membrane Technology

Emulsion liquid membrane was invented as an alternative of liquid/liquid extraction. ELM involves the application of extraction and stripping processes in the same stage and container, eliminating separate containers as available in conventional liquid/liquid extraction. The utilisation of organic solvent in liquid/liquid extraction could be minimised in emulsion liquid membrane, thus minimising the disposal of harmful wastewater. ELM system consists of external feed phase and internal dispersed phase. The external phase contains solute to be extracted in the internal stripping phase. Both phases are separated by thin-layer film, roles as barrier, thus enabling selective mass transfer from external phase into internal phase. Liquid membrane composed of organic solvent and surfactant to reduce the interfacial tension between the two phases. In case of facilitated transport ELM system, an extractant is needed to carry solute in the external phase through membrane phase towards internal stripping phase that acts as stripper in receiving the solute. Based on the phase of feed solution, ELM system could be available as water in oil in water (W/O/W) type or oil in water in oil (O/W/O) type. In W/O/W system, immiscible oil phase separates the aqueous phases while in

O/W/O system, the barrier of two oil phases is the immiscible water phase. Chakraborty *et al.*, [12] revealed that in term of mass transfer area, emulsion liquid membrane is very prospective due to the emulsion globules provide a huge mass transfer area of about $3000 \text{ m}^2/\text{m}^3$, make it beneficial for low solute concentration. Tiny emulsion globules are preferable in ELM system; however, considering the feasibility of demulsification process, optimal emulsion size must be determined. The prepared emulsion is then dispersed in the external feed phase to extract the solute. Mass transfer of solute from external feed phase through membrane phase into internal stripping phase takes place by diffusion. Concentration gradient of the solute in external feed phase and internal stripping phase triggers mass transfer process. Stirring the extraction system significantly increases the mass transfer rate. Although in facilitated transport the mass transfer process occurs by the support of extractant, gradient concentration of H^+ still have to be considered to prevent emulsion breaking.

Solutes transfer from the external aqueous phase into internal phase of emulsion droplets occurs through two mechanisms, i.e., type 1 and type 2 facilitations [13]. In type 1 facilitation, i.e. unfacilitated transport, the dissolved solute species transfer from external continuous phase into internal stripping phase. Inside the the internal phase, the solute reacts with the chemical reagents available in the phase and forms a product that is insoluble in the membrane phase, thus cannot diffuse back to external phase. It is therefore the solute concentration in the internal phase of ELM is effectively zero. Phenol removal from wastewater is an example of type 1 facilitation. Phenol from the continuous phase diffuses through oil membrane phase towards internal stripping phase in which it reacts with sodium hydroxide to form sodium phenolate. The formed ionic species is insoluble in the oil membrane phase, thus effectively entrapped in the internal aqueous phase. Phenol concentration in the internal phase is effectively zero. Illustration of unfacilitated transport is described in Figure 1. In the figure, "A" refers to solute to be extracted.

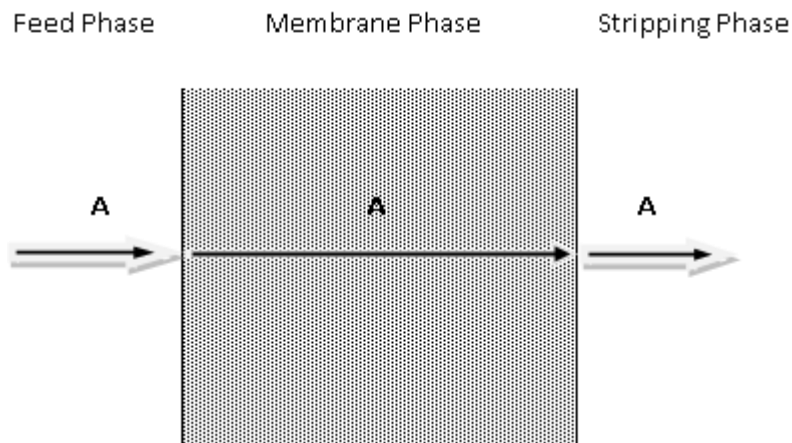


Fig. 1. Unfacilitated transport

Type 2 facilitation is a phenomenon in which solute transport is facilitated by extractant. The extractant compound, which is the extracting or complexing agent, dissolved in the organic phase used to carry the solute across the membrane. In this situation, the solute reacts with the carrier to form complexes that only soluble in the membrane phase. The solute-carrier complex diffuses into internal phase, then the stripping solution strip the metal ion. An example of this process is the removal of metal ions such as cadmium from wastewater by trioctylamine (TOA) [14]. Selectivity is also enhanced by carrier because under determined conditions; most extractants are specifically designed to extract specific metal ions. The metal ion, Cd^{2+} in the external continuous phase reacts with TOA in the oil phase to form an oil-soluble complex, $(\text{R}_3\text{NH})_2\text{CdCl}_4$. Concentrated sodium

hydroxide in the internal aqueous phase releases metal ions from the solute-carrier complex and transfer to internal phase, exchanging metal ions with protons.

In case of facilitated transport, solubility of solute in the membrane phase is not important because the solute will be carried by extractant, noted as "C", to dissolve through the membrane phase. The carrier must be insoluble in the feed phase or in the stripping phase. Moreover, carriers should be able to specifically and reversibly react with solutes. Transport mechanisms could occur in various types, depending on the nature of the carrier. Counter-transport mechanism occurs based on the ion exchange process takes place in the interface of membrane phase, the transfer of substance A, coupled with the transfer of counter ion of D, in the opposite direction, as shown in Figure 2. The solute can be transferred even in the opposite direction of the concentration gradient, by giving a higher counter ion concentration than that of solute concentration.

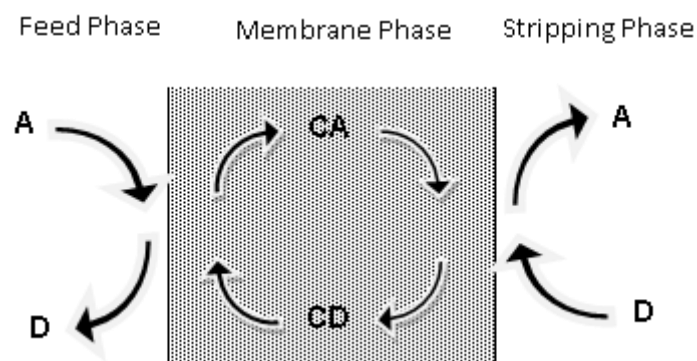


Fig. 2. Counter transport

The driving force of solute transfer in co-transport mechanism is triggered by the difference of concentration of solute "A". The solute can be transported in the opposite direction of concentration gradient. Schematically, co-transport mechanism in emulsion liquid membrane system is described in Figure 3.

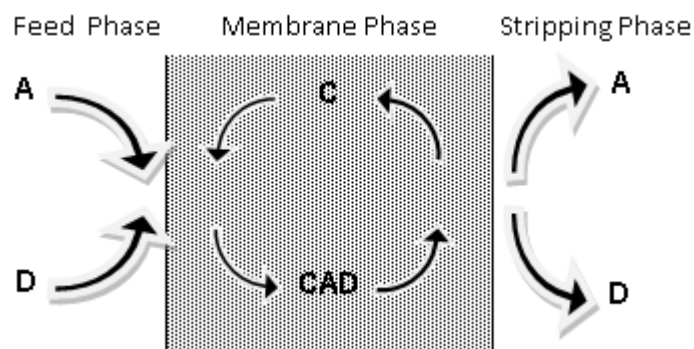


Fig. 3. Co-transport

An illustration of phenol extraction through emulsion liquid membrane system is revealed in Figure 4. It is seen that the system consists of two water phases, separated by thin layer liquid membrane, in this example represented by kerosene. The left water phase is wastewater contains phenols as contaminants, while the right side of water phase is internal stripping phase in form of sodium hydroxide solution. Since water is insoluble in the kerosene, only phenols could pass through the liquid membrane. Concentration difference of phenols in feed phase and internal phase triggers the diffusion of phenols into emulsion. Once reaching internal phase, phenols react with sodium

hydroxide to form sodium phenolate which is insoluble in kerosene thus cannot diffuse back into feed phase

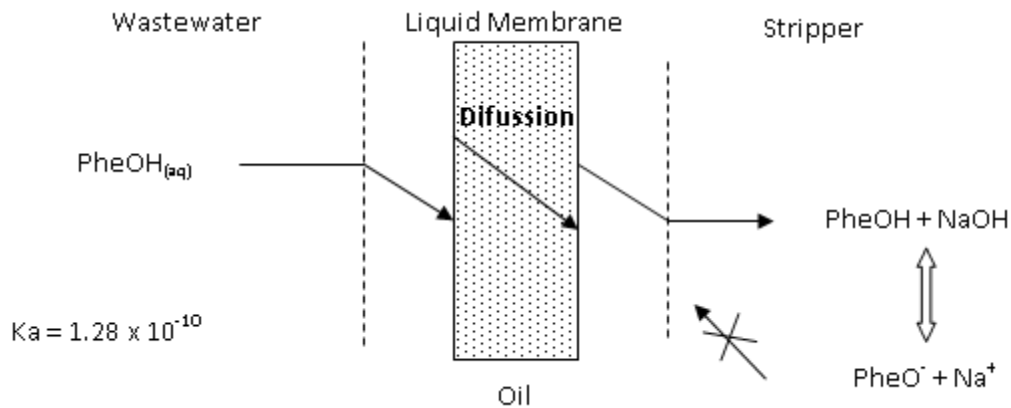


Fig. 4. Mechanism of phenols extraction using emulsion liquid membrane

Applications of conventional stirred tanks have been widely investigated for solute recovery under emulsion liquid membrane process. However, this method is still experiencing several problems. Better extraction rate could be achieved by applying high stirring speed which is detrimental to emulsion stability. Many researchers have concerned in optimisation study of membrane breakage and emulsion swelling [15-17]. Another problem comes from the difficulty of used emulsion breaking due to the production of too stable emulsion.

The design of Taylor-Couette column in the extraction under emulsion liquid membrane process was done to minimise emulsion instability by maintaining high extraction performance. ELM process within the TCC offers relatively low and uniform fluid shear thus preventing membrane breaking and emulsion swelling [18]. TCC is a system with two independent cylinders, move freely in two opposite direction. The solution is flowed in the gap of the cylinders. TCC provide higher contact area, mass transfer occurs along the cylinders thus significantly increase extraction rate at short extraction time. There were 18 principles regimes in flow between independently rotating cylinders found by Andereck *et al.*, [19]. The flow patterns were mapped out based on Reynolds number, for both inner and outer cylinders. Application of Taylor-Couette column in emulsion liquid membrane system was able to reach almost complete cadmium extraction in less than 3 mins [5], which is much more efficient than that of previous study by Li *et al.*, [20], in which about 91% of cadmium was recovered in 5 mins. Taylor-Couette column considered to be promising for minimising emulsion instability phenomenon. Ahmad *et al.*, [5] revealed that Taylor-Couette column was able to reduce emulsion swelling and membrane breakage of about 44% and 97%, respectively. This is a very significant finding for the scale up application of emulsion liquid membrane system.

3. Emulsion Formulation of Tar Removal

Emulsion liquid membrane has been an established method in recovering deficient solute concentration. However, emulsion stability is gained a significant concern from researchers. Emulsion instability phenomena in ELM system mostly caused by membrane breakage and emulsion swelling. Phenomena of emulsion instability lead to the decrease of overall process efficiency due to the release back of entrapped solute to the external feed phase. It is therefore, emulsion formulation and emulsification methods must be very well determined.

Liquid membrane composed of organic solvent, mixed with aqueous phase to produce emulsion. Surfactant is added to organic solvent to decrease interfacial tension of organic and aqueous phases.

The used equipment is among the factors determining the success of emulsification process. The others are emulsion composition, including type and concentration of surfactant, carrier, diluents and internal phase, as well as volume ratio of membrane to internal phase. Operating conditions such as emulsification time and probe position influence the quality of the produced emulsion.

Emulsion liquid membrane is a very selective method, that the emulsion is specially designed for specific solute. Tar is among the harmful component generated from gasification process. If the coke oven flue gas containing tar freely discharged into the atmosphere without any prior treatment, environmental pollution would be generated and health of human beings would be threatened. Previous studies on tar removal using emulsion liquid membrane were done under two types of ELM systems, i.e., oil in water in oil (O/W/O) [6-9]. Emulsion and water in oil in water (W/O/W) emulsion, depending on the types of feed phase solution.

Dong *et al.*, [6] extracted tar and dust in coke oven flue gas using emulsion liquid membrane. Effects of some parameters and operating conditions to tar and dust removal efficiency were investigated. Real tar was taken from coking plant and dissolved in xylene. The water phase feed solution was then extracted underwater in oil in water (W/O/W) emulsion system. An L-113B was used as surfactant and kerosene was used as organic solvent. Both of the liquids were then mixed to obtain the oil membrane phase, then distilled water as internal phase was added drop wise to the oil membrane phase and mixed using at a homogenizer speed of 1000 rpm for 15 mins to get a milky white colour W/O emulsion. Flow chart of simultaneous removal of tar and dust by emulsion liquid membrane is given in Figure 5.

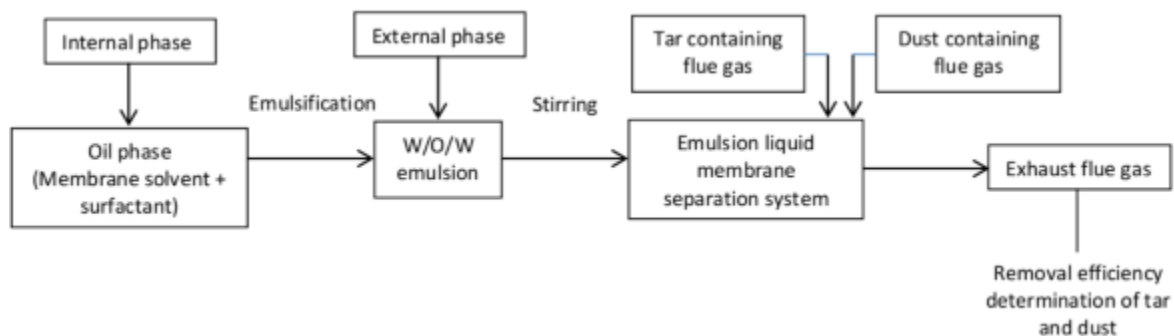


Fig. 5. Flow chart of simultaneous removal of tar and dust by emulsion liquid membrane [6]

Concentration of L-113B was varied at 1-5 vol. %. It was found that at L-113B concentration of 1 vol. %, tar removal efficiency was about 95%. The removal efficiency increased to be about 98% at surfactant concentration of 3 vol. %, further increment of surfactant concentration until 5 vol. % insignificantly resulted in difference of tar removal efficiency. Low surfactant concentration is not sufficient to cover the whole internal phase solution thus resulted in high membrane instability. Contrarily, excessive surfactant improves the resistance of interface of external and membrane phases that inhibits mass transfer process. More surfactant also potential in improving emulsion swelling by the water transport phenomenon [21]. Volume ratio of membrane to internal phase was investigated in the range of ratio 3/7 to 7/3. It was revealed that tar removal efficiency increases as the increase of volume ratio of membrane to internal phase from 3/7 to 1/1. The highest tar removal efficiency was about 98%. Further increase of volume ratio of membrane to internal phase to 7/3 leads to the decrease of tar removal efficiency to be about 97%. This is in accordance with the finding of Abismail *et al.*, [22] that volume ratio of membrane to internal phase determines emulsion size. Exact amount of membrane solution must be provided to ensure the coverable of internal phase solution. Otherwise, large emulsion globules having thin wall that is very risky in facing membrane breakage would be produced. However, excessive membrane solution resulted in thick emulsion wall

which is not beneficial for mass transfer due to high interfacial resistance and large diffusional path. Study on effect of emulsification speed to tar removal efficiency was carried out at 2000 rpm to 6000 rpm with interval of 1000. The results showed that emulsification speed of 2000 rpm to 4000 rpm significantly enhanced tar removal efficiency. More acceleration in emulsification speed lowered removal efficiency to be about 97%. Emulsification speed highly determines emulsion size. Slower emulsification speed produces relatively bigger emulsion. Higher emulsification speeds generate smaller emulsion size and higher emulsion number that in turn increasing removal efficiency. However, excessive speed acceleration triggers emulsions coalescence, which enlarges emulsion diameter [23].

Zhang *et al.*, [7] developed tar removal by emulsion liquid membrane process. L-113B and kerosene were used as surfactant and organic solvent, respectively. The internal and external phase solution was distilled water. A high-speed stirrer was occupied to produce emulsion. The coke flue gas was flowed into separation vessel to let tar extracted. Pre weighted cotton was put in the pipe of discharge gas. At the end of the process, the cotton weight was measured to determine tar removal efficiency. Surfactant concentration was varied in the range of 1-5 vol. %. Significant increment of tar removal efficiency was seen from surfactant concentration of 1-3 vol. %. Further addition of surfactant gave no more increase in tar removal efficiency. Profile of tar removal efficiency as a function of emulsification speed was studied at 2000 – 5000 rpm. The highest tar removal efficiency of about 97% was achieved by system with emulsification speed of 4000 rpm. Lower and higher emulsification speed resulted in lower tar removal efficiency. They revealed that higher emulsification speed provided better mixing of membrane and internal phases thus produced smaller emulsion with better emulsion stability as well as larger mass transfer interfacial areal. Membrane swelling was found at system with emulsification speed beyond 4000 rpm. The influence of volume ratio of membrane to internal phase was examined at 1/4 to 7/3. Emulsion viscosity is higher at larger volume ratio, leading to the formation of thicker emulsion membrane that is relatively stable. However, volume ratio of membrane to internal phase of higher than 1/1 caused the reduction of tar removal efficiency. Further experiment was continued at volume ratio of membrane to internal phase at 1/1.

Shimada *et al.*, [9] studied the separation of absorption oil by emulsion liquid membrane. Absorption oil was applied as external feed phase solution. Membrane breakage rate in some permeation runs was measured by adding decane. Few types of surfactant were used as liquid membrane, namely saponin, sorbitan monostearate, sorbitan monooleate, Polyoxyethylene oreyl ether (POE), Polyoxyethylene stearyl ether (PSE), Polyethylene glycol monocethyl ether (PGME). Toluene was employed as organic solvent. A commercial high-speed homogenizer (SMT Multi Disperser, SMT Corp.) was intensively agitated to prepare the emulsion. Effects of surfactant on mass fraction of quinolone in extract phase was tested. Profile of mass fraction along the time was presented. Permeation was carried out in the interval of 0-0.044 hours. Mass fraction increased from 0-0.02 hour and remained constant until the end of permeation process. There were slight differences of mass transfer rate of quinoline, increased in the order of saponin, PSE, Tween 60, Tween 80, PGME, and POE. This is due to each type of surfactant defines emulsion size and characteristics [24]. Higher mass transfer rate was generated by smaller emulsion diameter. The effects of surfactant concentration on the permeation of quinolone were tested in concentrations of 0.005 and 0.03. The mass transfer rate of quinoline increased with concentration of surfactant. It mainly because of the enlargement of interfacial area of emulsion and external solvent phases by the decrease of an emulsion drop diameter and that between the emulsion and internal raffinate phases increased due to the decrease of an inner oil droplet diameter, respectively.

The separation enhancement of coal tar absorption oil was studied by Habaki *et al.*, [8]. They used absorption oil as feed solution and toluene as solvent. The aqueous membrane solution composed of ion-exchanged water, saponin as surfactant, and one additive of MeOH, EG, DEG, TEG or BuD. Emulsion preparation was done by stirring feed absorption oil and aqueous membrane solution in a commercially available homogenizer. The prepared emulsion was brought into contact with toluene using a Pyrex glass stirring vessel equipped with a six-flat-blade turbine type impeller and four baffles. The nitrogen heterocyclic compounds selectively extracted through liquid membrane and could be separated from the homocyclic compounds. Extraction of quinoline as heterocyclic component was much larger than those of dimethylnaphthalene as homocyclic component, while extraction of other nitrogen heterocyclic component was also higher than those of dimethyl naphthalene with any additive. The yields and permeation rates of all components could be enhanced by the use of most additives compared to permeation through membrane solution without additive. Permeation rates were only slightly enhanced by application of 1,3 butanediol and ethylene glycol while distribution coefficients increased by these additives. Larger yields and permeation rates were obtained by system prepared with methanol and di ethylene glycol than those of tri ethylene glycol and 1,3 butanediol. However, higher distribution coefficients were given by emulsion prepared by methanol, tri-ethylene glycol and 1,3 butanediol than those of di-ethylene glycol and ethylene glycol. Among heterocyclic components, quinoline provided the highest overall volumetric permeation coefficients, followed by those of isoquinoline and indol. The overall permeation coefficients of quinoline rapidly decreased along permeation time, while overall permeation coefficients of dimethyl naphthalene gradually decreased along permeation time.

In study of Putrawan *et al.*, [10], emulsifier consisted of a high-speed homogenizer (NITI-ON NS-50, 20TP, 20G), an emulsifying vessel, and a flow cell (FO-20 type) used to produce emulsion. Schematic diagram of emulsion liquid membrane process to recover dimethyl naphthalene from light cycle oil is shown in Figure 6.

The vessel served as a pre-mixer and the homogenizer agitated the premixed O/W emulsion through the flow cell. The O/W emulsion composed of liquid membrane (contained water, sulfolane, and saponin) and hexane, pentane and heptane as solvent. They revealed that lighter solvent needed lower total boiler duty and less equilibrium stages, because the lighter the solvent, the greater the difference in boiling point of solvent and permeate or raffinate. However lighter solvent gave lower yield of dimethyl naphthalene. Despite the easy recovery, a very light compound is not desirable to be used as solvent. System with heptane as solvent was able to recover more than 80% DMN, while that of pentane only succeeded in recovering less than 50% DMN. It triggered by the difference of inward permeation coefficient of solvent. Lighter solvent generated higher inward permeation coefficient of solvent, showed that more solvent permeated from the extract phase into the feed phase. It is therefore, the more dilute the feed and the lower the driving force of the components transferring from feed phase into extract phase. Solvent permeation into feed phase not only diluted the feed but also decreased solvent capacity. Much more solvent permeated into feed phase by the application of pentane as solvent. Solvent selection must regard to total boiler duty and yield of dimethyl naphthalene as well as design of distillation tower. In terms of total boiler duty, pentane performed the best solvent. But considering that cooling water temperature reaches 40°C on a hot summer day, it is challenging to design condensers of distillation tower due to normal boiling point of pentane is 36°C. Although heptane resulted in the highest yield of dimethyl naphthalene, but it also required the greatest total boiler duty. After taking into account the total boiler duty, yield of dimethyl naphthalene, and cooling water temperature, seen that hexane was the best solvent.

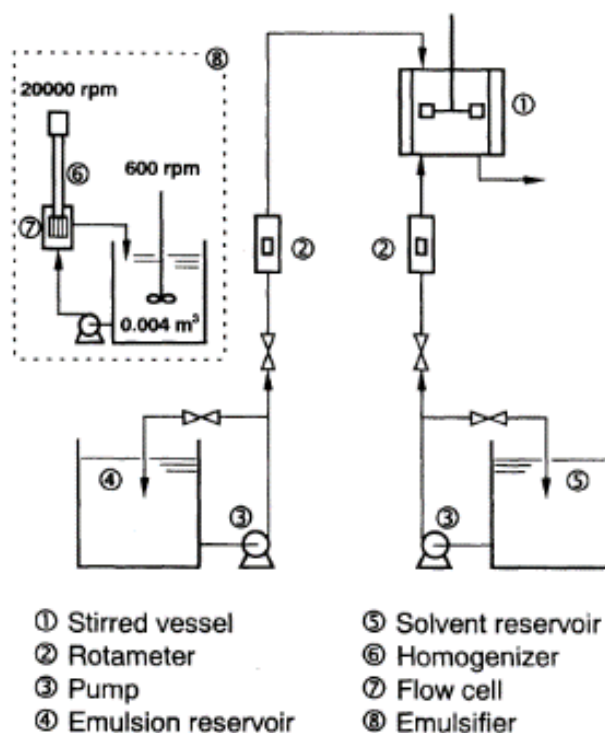


Fig. 6. Schematic diagram of emulsion liquid membrane process to recover dimethyl naphthalene from light cycle oil [10]

Egashira *et al.*, [11] used a high-speed homogeniser and a flat blade turbine to produce emulsion. The liquid membrane was stabilised by saponin at concentration of 0.001-0.003. Two types of solvent mixtures were employed, i.e., isooctane-nonane and hexane-nonane. Two types of feed phase solution were also used, i.e., benzene-hexane-decane mixture and toluene-heptane-decane mixture. It was assumed that decane and nonane did not permeate and acted as tracers to measure rates of membrane breakage and mechanical entrainment. A centrifugal particle size analyser and an optical microscope were applied to determine inner droplet diameter. It was found that high-speed homogeniser was able to produce tiny emulsion droplets of about 2×10^{-6} m in diameter while much bigger emulsion droplet of 1×10^{-5} m in diameter was produced by flat blade turbine. The same tendency applied in the permeation using both equipment. Permeation process under high speed homogeniser generated emulsion drop of about 1×10^{-5} m in diameter while flat blade turbine generated emulsion drop of 1.6×10^{-4} m in diameter. Net permeation rate was estimated by taking into account the breakage and entrainment rates. It was revealed that no serious membrane instabilities occurred in permeation process, even in the application of high-speed homogeniser. Separation selectivity in permeation under high speed homogeniser was higher than that of permeation using flat blade turbine. This is related to the fact that high speed homogeniser provided much smaller emulsion drop that in turn gave larger interfacial mass transfer area. Larger inner droplet resulted in higher selectivity. The experiment finding supported the simulation that emulsion liquid membrane selectivity could be improved by decreasing the number of inner droplets. Multi-layer liquid membrane model for permeation of hydrocarbon through O/W emulsion drop is illustrated in Figure 7.

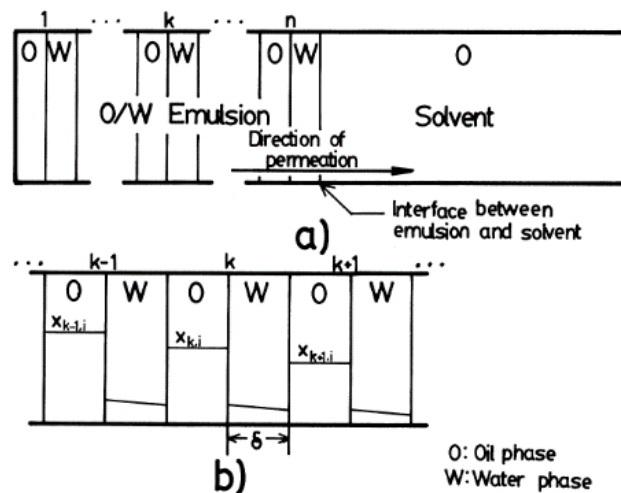


Fig. 7. Multi-layer liquid membrane model for permeation of hydrocarbon through O/W emulsion drop [11]

4. Effect of Permeation Process on Tar Removal

Some parameters and operation conditions used in extraction process determine the process efficiency. Extraction efficiency is profoundly affected by volume ratio of feed to emulsion phase, pH of external phase, and initial concentration of feed solution. Operating condition such as stirring rate influences the extraction rate. Solute concentrations at different parameters and operating conditions are described in time profiles.

Experiment of Dong *et al.*, [6] on tar and dust removal was carried out in various initial tar concentration, in the interval of 11.62 to 46.48 mg/L. The tar was diluted in xylene and the determination of tar concentration was done by the aid of spectrophotometer at wavelength of 290 nm. Pre-weighted dry degreasing cotton was placed in the exhaust gas absorption bottle to measure tar and dust removal efficiency. After the extraction process, the cotton was soaked in the xylene to dissolve the absorbed tar. The tar concentration in the xylene was then measured using spectrophotometer. To determine the influence of volume ratio of emulsion to external phase on tar removal efficiency, study was carried out at ratio 1/7 to 1/3. Increase in tar removal efficiency was seen by the increase of volume ratio of emulsion to external phase from 1:7 to 1:5. Addition of emulsion provides more effective emulsion droplets thus increasing mass transfer area [25]. However, the increase of volume ratio of emulsion to external phase from 1:5 to 1:3, tar removal efficiency was almost constant. Datta *et al.*, [26] revealed that excessive treat ratio inhibits the emulsion dispersion in external phase solution. It leads to the sharp decrease of surface contact area between emulsion phase and external feed phase, results in the decrease of solute transfer rate. Lower treat ratio provides more space for the emulsion to freely disperse that more surface contact area between emulsion phase and external feed is available.

Research of Zhang *et al.*, [7] applied the variation of volume ratio of emulsion to feed phase, gas flow rate, and stirring speed to tar removal efficiency. They found that volume ratio of emulsion to external phase directly affected emulsion dispersion in external phase thus governed mass transfer surface. Tar removal efficiency increased remarkably by increasing volume ratio of emulsion to external phase from 1:8 to 1:5. Capacity of membrane and internal phase in extracting and stripping the solute increased at higher treat ratio. Enhancement of emulsion hold up has also happened. In facilitated transport, the availability of more extractant at higher treat ratio is favourable as well for the extraction process. But, further increase of volume ratio of emulsion to external phase from 1:5

to 1:3, resulted in no difference of tar removal efficiency. It can be explained that enhancement of emulsion holds up would in turn enlarging emulsion globule and shifting the globule size distribution toward the higher end of the spectrum. Lower external mass transfer area was generated by bigger emulsion globule [27]. Moreover, higher volume ratio of emulsion to external phase more likely result in emulsion liquid membrane swelling and the larger the volume ratio of emulsion to external phase require the higher operational cost. Therefore, 1:5 was selected as the optimum volume ratio of emulsion to external water phase.

Effect of stirring velocity on permeation of quinolone was investigated by Shimada *et al.*, [9] It was found that mass transfer rate of quinoline increased with stirring velocity. The permeation coefficients of nitrogen compounds were ten times higher than those of the homocyclic compounds. It increased with stirring intensity and decreased with operation time. The decrement of permeation coefficients of quinoline was more remarkable than those of dimethylnaphtalene. It was mainly attributed to the decrease of permeation coefficients by the unfavourable concentration profile developing in emulsion drops with permeation. There was a decrease of permeable compounds concentration than that of nonpermeable ones with permeation in inner oil droplets near solvent phase. In turn, the permeation rate and the permeation coefficients were also decreased. Initially, separation selectivity of dimethyl naphthalene was more than 40 and the nitrogen compounds could be selectively separated under any conditions studied. The separation selectivity of dimethyl naphthalene as well as other nitrogen compounds decreased with time because permeation coefficients of nitrogen compounds decreased more than permeation coefficients dimethyl naphthalene.

Habaki *et al.*, [8] separated tar from absorption oil using O/W/O emulsion liquid membrane system. Permeation was started at $t=0$ h and the stirring was continued for the specified operating time. After permeation, emulsion and extract were separated by a separating funnel. Extract analysis was done by the aid of a gas chromatograph thus extract composition was clearly found. Mass balance equation was able to calculate raffinate composition. Application of MeOH in concentration of 0.25 provided higher extraction for nitrogen heterocyclic compounds than that of nitrogen homocyclic compounds.

Egashira *et al.*, [11] separation selectivity in permeation under high speed homogeniser increased with increasing stirring velocity. It was experimentally confirmed that overall permeation coefficient of aromatic compounds increased by the increase of the number of emulsion layers while overall permeation coefficient of paraffin compounds decreased by the increase of the number of emulsion layers. Separation selectivity of the compound was inversely proportional with the number of emulsion layers. The obtained experimental values of permeation coefficient of aromatic and paraffin compounds roughly fitted to those in the model thus validate the simulation.

In the experiment of Putrawan *et al.*, [10] that separate dimethyl naphthalene from light cycle oil, it was found that yield of dimethyl naphthalene increased with stirring rate, number of permeation stages, and volume of vessel. At high values of these variables, the system was able to recover about 68% dimethyl naphthalene in purity of 92%. Yield of dimethyl naphthalene was decreased by permeator reflux ratio; however, total boiler duty was hardly affected. Favourable conditions were found at lower permeator reflux ratio. In order to increase yield of dimethyl naphthalene by ignoring energy source, it is recommended to operate the process at high flow rate of solvent to feed, high stirring rate, high number of permeation stages, high volume of vessel and low permeator reflux ratio.

Summary of the important findings related to application of emulsion liquid membrane system for tar removal is given in Table 1.

Table 1
Application of emulsion liquid membrane for tar removal studies

Reference	Type of tar	Type of ELM	Tar removal efficiency
Zhang <i>et al.</i> , [7]	Coke oven flue gas	W/O/W	97%
Dong <i>et al.</i> , [6]	Coke oven flue gas	W/O/W	98%
Shimada <i>et al.</i> , [9]	Coal tar absorption oil	O/W/O	Given in mass fraction
Habaki <i>et al.</i> , [8]	Coal tar absorption oil	O/W/O	Given in mass fraction
Putrawan <i>et al.</i> , [10]	Dimethyl naphthalene from light cycle oil	O/W/O	80%

5. Conclusions

Application of ELM for tar removal has been described. ELM offers a promising method for recovery of tar contained in producer gas generated from gasification/pyrolysis of biomass. Among the ELM transport mechanism, unassisted transport seemed to be the most suitable process for tar removal. In order to successfully recover tar, the consideration not only depends on the selection of suitable emulsification method but also the emulsion formulation to produce selective emulsion including both types and concentration of the surfactant and the diluent, in accordance with tar to be recovered. Moreover, volume ratio, pH of external phase, initial concentration of feed solution, and stirring speed were the main parameters that profoundly affect removal efficiency. The choice of extraction equipment is also important by the emulsion instability issue. The current upcoming technology is Taylor-Couette column that is believed to solve the problem. So that, utilisation of Taylor-Couette column for further tar recovery study will provide new insight, to ensure high process efficiency by minimising emulsion instability phenomenon.

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References

- [1] Belgiorno, V., G. De Feo, C. Della Rocca, and R. M. A. Napoli. "RMA.: Energy from gasification of solid wastes." *Waste Management* 23, no. 1 (2003): 1-15.
[https://doi.org/10.1016/S0956-053X\(02\)00149-6](https://doi.org/10.1016/S0956-053X(02)00149-6)
- [2] Yusoffa, Nur Sakinah Mohd, Maizirwan Mel, Wan Bazli Wan Ishak, and Azlin Suhaida Azmi. "Production of Coconut Shell Liquid Smoke from Pilot Plant of Pyrolysis Process." *Journal of Advanced Research in Biofuel and Bioenergy* 1, no. 1 (2017): 21-26.
- [3] Devi, Lopamudra, Krzysztof J. Ptasinski, and Frans J.J.G. Janssen. "A review of the primary measures for tar elimination in biomass gasification processes." *Biomass and Bioenergy* 24, no. 2 (2003): 125-140.
[https://doi.org/10.1016/S0961-9534\(02\)00102-2](https://doi.org/10.1016/S0961-9534(02)00102-2)
- [4] Anis, Samsudin, and Z. A. Zainal. "Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review." *Renewable and Sustainable Energy Reviews* 15, no. 5 (2011): 2355-2377.
<https://doi.org/10.1016/j.rser.2011.02.018>
- [5] Ahmad, A. L., Adhi Kusumastuti, MMH Shah Buddin, C. J. C. Derek, and B. S. Ooi. "Emulsion liquid membrane based on a new flow pattern in a counter rotating Taylor-Couette column for cadmium extraction." *Separation and Purification Technology* 127 (2014): 46-52.
<https://doi.org/10.1016/j.seppur.2014.02.029>
- [6] Dong, Pengxiong, Junjie Zhang, Yekun Sun, and Hongxia Li. "Simultaneously Removal of Tar and Dust by Emulsion Liquid Membrane." In *IOP Conference Series: Earth and Environmental Science*, vol. 267, no. 3, p. 032083. IOP Publishing, 2019.
<https://doi.org/10.1088/1755-1315/267/3/032083>

- [7] Zhang, Junjie, Pengxiong Dong, Chunying Li, and Hongxia Li. "Removal of tar from coke oven flue gas by emulsion liquid membrane." In *IOP Conference Series: Earth and Environmental Science*, vol. 295, no. 5, p. 052023. IOP Publishing, 2019.
<https://doi.org/10.1088/1755-1315/295/5/052023>
- [8] Habaki, Hiroaki, Dejin Bi, Yoshiyuki Shimada, and Ryuichi Egashira. "Enhancement of permeation rate of nitrogen heterocyclic compounds for emulsion liquid membrane separation of coal tar absorption oil." *Journal of Chemical Engineering of Japan* 47, no. 3 (2014): 254-260.
<https://doi.org/10.1252/jcej.13we153>
- [9] Shimada, Yoshiyuki, Dejin Bi, Hiroaki Habaki, and Ryuichi Egashira. "Mass Transfer Rate in Separation of Coal Tar Absorption Oil by Emulsion Liquid Membranes." *Journal of Chemical Engineering of Japan* 46, no. 6 (2013): 376-382.
<https://doi.org/10.1252/jcej.12we250>
- [10] Putrawan, I. Dewa Gede Arsa, Shunji Oshima, Hiroaki HABAki, Ryuichi Egashira, and Junjiro Kawasaki. "Recovery of dimethylnaphthalene isomers from light cycle oil by O/W/O emulsion liquid membrane process." *Journal of The Japan Petroleum Institute* 42, no. 3 (1999): 136-144.
<https://doi.org/10.1627/jpi1958.42.136>
- [11] Egashira, Ryuichi, Hirotaka Tanno, Satoru Kato, and Junjiro Kawasaki. "A simple way for the improvement of separation selectivity of hydrocarbons by O/W/O emulsion liquid membrane." *Journal of chemical engineering of Japan* 28, no. 1 (1995): 38-45.
<https://doi.org/10.1252/jcej.28.38>
- [12] Chakraborty, Mousumi, Chiranjib Bhattacharya, and Siddhartha Datta. "Emulsion liquid membranes: Definitions and classification, theories, module design, applications, new directions and perspectives." In *Liquid Membranes*, pp. 141-199. Elsevier, 2010.
<https://doi.org/10.1016/B978-0-444-53218-3.00004-0>
- [13] Jilska, Perera M., and Stevens W. Geoff. "Use of emulsion liquid membrane systems in chemical and biotechnological separations." *Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications* (2009).
<https://doi.org/10.1201/9781420009484.ch25>
- [14] Kusumastuti, Adhi, Nur Qudus, Samsudin Anis, and Abdul Latif Ahmad. "Emulsion Liquid Membrane for Cadmium Removal: Determination of Liquid Membrane Components." *Journal of Physical Science* 29 (2018): 227-242.
<https://doi.org/10.21315/jps2018.29.s2.18>
- [15] Ahmad, A. L., Adhi Kusumastuti, C. J. C. Derek, and B. S. Ooi. "Emulsion liquid membrane for cadmium removal: Studies on emulsion diameter and stability." *Desalination* 287 (2012): 30-34.
<https://doi.org/10.1016/j.desal.2011.11.002>
- [16] Ahmad, A. L., A. Kusumastuti, C. J. C. Derek, and B. S. Ooi. "Emulsion liquid membrane for heavy metal removal: An overview on emulsion stabilization and destabilization." *Chemical Engineering Journal* 171, no. 3 (2011): 870-882.
<https://doi.org/10.1016/j.cej.2011.05.102>
- [17] Djenouhat, Meriem, Oualid Hamdaoui, Mahdi Chiha, and Mohamed H. Samar. "Ultrasonication-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane: Part 1: Membrane stability." *Separation and Purification Technology* 62, no. 3 (2008): 636-641.
<https://doi.org/10.1016/j.seppur.2008.03.018>
- [18] Park, Yonggyun. "Development and optimization of novel emulsion liquid membranes stabilized by non-newtonian conversion in taylor-couette flow for extraction of selected organic and metallic contaminants." *PhD diss., Georgia Institute of Technology*, 2006.
- [19] Andereck, C. David, S. S. Liu, and Harry L. Swinney. "Flow regimes in a circular Couette system with independently rotating cylinders." *Journal of Fluid Mechanics* 164, no. 3 (1986): 155-183.
<https://doi.org/10.1017/S0022112086002513>
- [20] Li, Quanmin, Qi Liu, Kean Li, and Shenyang Tong. "Separation study of cadmium through an emulsion liquid membrane." *Talanta* 44, no. 4 (1997): 657-662.
[https://doi.org/10.1016/S0039-9140\(96\)02098-X](https://doi.org/10.1016/S0039-9140(96)02098-X)
- [21] Yan, Jun, and Rajinder Pal. "Isotonic swelling behavior of W/O/W emulsion liquid membranes under agitation conditions." *Journal of Membrane Science* 213, no. 1-2 (2003): 1-12.
[https://doi.org/10.1016/S0376-7388\(02\)00501-X](https://doi.org/10.1016/S0376-7388(02)00501-X)
- [22] Abismail, B., Jean P. Canselier, Anne M. Wilhelm, Henri Delmas, and Christophe Gourdon. "Emulsification by ultrasound: drop size distribution and stability." *Ultrasonics Sonochemistry* 6, no. 1-2 (1999): 75-83.
[https://doi.org/10.1016/S1350-4177\(98\)00027-3](https://doi.org/10.1016/S1350-4177(98)00027-3)

- [23] Chakraborty, Mousumi, and Hans-Jörg Bart. "Emulsion liquid membranes: Role of internal droplet size distribution on toluene/n-heptane separation." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 272, no. 1-2 (2006): 15-21.
<https://doi.org/10.1016/j.colsurfa.2005.07.002>
- [24] Kobayashi, Isao, Mitsutoshi Nakajima, and Sukekuni Mukataka. "Preparation characteristics of oil-in-water emulsions using differently charged surfactants in straight-through microchannel emulsification." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 229, no. 1-3 (2003): 33-41.
<https://doi.org/10.1016/j.colsurfa.2003.08.005>
- [25] Chiha, Mahdi, Mohamed H. Samar, and Oualid Hamdaoui. "Extraction of chromium (VI) from sulphuric acid aqueous solutions by a liquid surfactant membrane (LSM)." *Desalination* 194, no. 1-3 (2006): 69-80.
<https://doi.org/10.1016/j.desal.2005.10.025>
- [26] Datta, S., P. K. Bhattacharya, and N. Verma. "Removal of aniline from aqueous solution in a mixed flow reactor using emulsion liquid membrane." *Journal of Membrane Science* 226, no. 1-2 (2003): 185-201.
<https://doi.org/10.1016/j.memsci.2003.09.003>
- [27] Sengupta, Bina, Ranjan Sengupta, and N. Subrahmanyam. "Process intensification of copper extraction using emulsion liquid membranes: Experimental search for optimal conditions." *Hydrometallurgy* 84, no. 1-2 (2006): 43-53.
<https://doi.org/10.1016/j.hydromet.2006.04.002>