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Liquid fuel synthesis in microreactors: A review

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The demand for energy is continuously increasing worldwide. This places a constant strain on the production and availability of fossil fuels which most current energy is based on. Thus, alternative sources of energy (non-fossil based) are urgently needed to produce liquid fuels. However, conventional technologies and reactors used for these alternative processes have been associated with mass and heat transfer, long reaction times and extreme temperatures and pressures. To address these limitations, microreactors have been developed and utilised over the past decade, and have been proven to increase product yields, reduce residence time and product selectivity when compared to conventional reactors. This paper provides an in-depth review of the liquid fuel production routes over the last decade, and highlights the advantages of microreactors that have been successfully employed to overcome some of the issues faced with conventional bulk reactors.

1. Introduction

Liquid fuels produced from fossil fuels, such as petroleum and diesel, are the primary source for energy in modern times. These fuels account for approximately 97% of the global fuel production[1]. The world demand for fuel is increasing at an annual rate of 0.7%, due to the exponential increase of the global population. Liquid fuels are used to cover this demand mainly for power, heat and transportation purposes. Conventional production of liquid fuels is heavily reliant on crude oil, which provides up to 94% of the energy used in the transportation industry[2]. In its raw state, crude oil has limited use. Nonetheless, when processed and upgraded to be used as a feedstock for refineries, it yields a range of useful products for industry and end-users in the form of petroleum refined products (e.g. fuel gas, gasoline, naphtha, kerosene, liquefied petroleum gas (LPG), diesel, jet (aviation) fuel oil and bitumen)[3]. Refining of petroleum employs physical processes and chemical reactions to yield various products that are essential, in terms of liquid fuels. A study conducted by the world energy council shows that the demand for lighter petroleum products and diesel is rapidly increasing due to the increasing number of vehicles used globally[4].

Considering the increased demand for liquid fuel, and the concerns associated with the depletion of natural resources (e.g. fossil fuels), the high dependency on crude oil for the production of energy has raised concerns within the industry. This has prompted and led to the development of renewable liquid fuels which are able to replace conventional petroleum and diesel for transportation purposes[5]. The alternative, renewable fuels can be obtained from natural gas, biomass or waste, through an initial conversion to syngas, followed by different catalytic processes for the conversion to liquid fuels. As these synthetic fuels have similar compositions and characteristics to conventional petroleum fuels, they can easily replace conventional fuels[6-8].

Production of these renewable liquid fuels were initially dependent on conventional reactor processes. However, microreactor processing and operation has attracted large attention in recent years due to its potential in intensifying the production of these alternative liquid fuels[9]. In addition, the technological advancements in catalysis, separation process and developments in micro-reaction engineering made on-site conversion technologies for processing and production of synthetic liquid fuels an interesting and viable alternative[10]. Their potential in revolutionising the field of synthetic liquid fuel production has already been demonstrated in the production of biofuels, such as methanol from the Fischer-Tropsch (FT) process and from natural gas[11].

Microreactors have also demonstrated significant higher fuel yields in comparison to conventional reactors. They have also

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shown better economic feasibility, due to their ability of allowing reactions to take place under milder conditions[7] when compared to conventional processes. Lerou et al.[12] assessed the techno-economic advantages of using microreactors in comparison to conventional macroscopic reactor units. It was noted that small channel dimensions lead to a higher mass and heat transfer, which maximises the catalyst's lifespan and generates higher product yield. In addition, the dimensions of the microreactors components lead to ease of construction and operation. Consequently, field installation takes place faster and the overall capital investment of the project is considered more lucrative than typical installations. Furthermore, overall project capital utilisation can be improved by adding or removing microreactor components to increase or eliminate the plant capacity on an incremental basis[12-13]. Many studies have shown promising results for liquid fuel synthesis in micro-structured reactors such as micro-channel reactors, packed bed microreactors and micro-plasma reactors. These were used to synthesise various liquid fuels comparable to commercial gasoline and diesel used in the energy and transportation sectors.

This review will offer a concise introduction to the different routes available to produce liquid fuels, followed by the challenges faced in current conventional units and reactors processing for fuel production purposes. The advantageous properties of microreactors will then explained, which will lead to a detailed review of the microreactors used, highlighting the benefits of doing so and how they overcome the problems faced with the conventional reactors. Finally, the operational variables that affect production yield in a microreactor system will be emphasised and discussed.

2. Liquid fuel synthesis routes

Liquid fuels are most commonly obtained from crude oil, which occurs naturally and is comprised of gaseous, liquid and solid hydrocarbons. Natural gas is typically present with crude oil, in the form of associated gas within the upper sections of the oil bearing strata. Liquid fuels obtained from crude oil involve well established conventional production processes. It is often referred to as conventional oil[14]. Unconventional oils are often derived from coal using direct or indirect coal liquefaction processes, biomass to biofuel technologies and gas to liquid (GTL) processes. Producing fuels in this way are cleaner as toxic compounds such as sulphur and mercury are extracted from the syngas before the liquid fuel production process. As a result, cleaner liquid fuels with lower toxic emissions are produced, as opposed to conventional petroleum and diesel fuels. These unconventional fuels are produced by the Fischer-Tropsch (FT) process or methane to methanol processes.

2.1 Gas-to-liquid

Natural gas, prior to its refinement, consists of a combustible mixture of various hydrocarbons. This hydrocarbon mixtures constitute mainly methane gas (CH_4) with traces of ethane, propane, butane and pentane. However, in its purest form, natural gas contains almost pure CH_4. Using CH_4 as a feedstock to synthesise liquid fuels has gained increasing attention. This technique has been regarded as a clean and abundant alternative to crude oil. Natural gas can be converted to liquid fuels using indirect technologies which has two routes. The first one uses the FT process to directly produce liquid fuels (Fig.1). The second one converts CH_4 to methanol which is further converted to liquid fuels. The direct conversion of CH_4 to liquid fuels consists of the oxidative coupling of CH_4 to produce olefin products such as ethylene. These products can then be further converted to liquid fuels using catalytic oligomerisation processes[15].

The two indirect routes mentioned above for the application of CH_4 to a liquid fuel, involve more specifically the production of synthetic gas (syngas), which consists of carbon monoxide (CO) and hydrogen (H_2). The production of syngas involves three processes, which can be used either individually, or in combination. The three processes are steam reforming, carbon dioxide (or dry) reforming and partial oxidation of gaseous or liquid hydrocarbons, and although each process has its own advantages and disadvantages, the most favoured method tends to be partial oxidation. Steam reforming of CH_4 is a highly developed chemical process for the production of syngas which subsequently generates methanol; it involves the conversion of CH_4 and steam (H_2O) into H_2 and CO (eq. 1).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \ (\Delta H_{298K} = 206 \ kJ/mol) \quad (1)$$
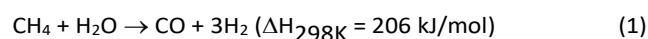
The partial oxidation reaction is also slightly exothermic; this process, however, requires the use of oxygen or air and it involves the total combustion of part of the CH4 over catalysts (eq. 2).

$$CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \quad (\Delta H_{298\,K} = -35 \ kJ/mol) \quad (2)$$
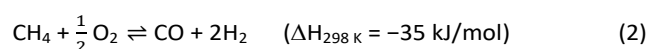
This is then subsequently followed by the reforming of the remaining CH_4 with CO_2 and water to produce CO_2 and H_2.

These reactions are accompanied by the exothermic water gas shift (WGS) reaction (eq. 3), which can be used to adjust the H_2/CO ratio. The products produced are CO_2 and H_2[16-17].

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \ (\Delta H_{298K} = -41.2 \ kJ/mol) \quad (3)$$
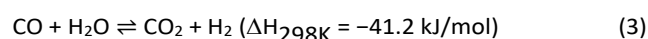
Methanol can then be produced from syngas, and the reaction is typically performed over a heterogeneous catalyst, such as co-precipitated $Cu/ZnO/Al_2O_3$, which is a reduced form of

$CuO/ZnO/Al_2O_3$. The reactions that take place for methanol synthesis are[15]:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (4)$$

$$CO_2 + 3H_2O \rightleftharpoons CH_3OH + H_2O \qquad (5)$$
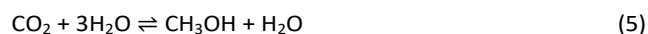
The synthesis of liquid fuels using methanol can be generated from the methanol-to-gasoline (MTG) process which uses a H-ZSM-5 zeolite catalyst, and was developed by Mobil©. This process predominantly produces gasoline; however, a variation of the process can produce distillate fuel as well. The process generates a high-octane gasoline which is rich in aromatics. The methanol-to-olefin (MTO) process developed can be used to produce chemicals such as ethylene and other light saturated hydrocarbons from methanol. The process uses a zeolite catalyst to convert the methanol to give very high yields of olefins, which can oligomerise and crack to form propylene. Methanol produced from methane can also be used to synthesise the fuel dimethyl ether (DME), which is an appealing fuel to use with diesel engines due to its lack of sulphur and particulate emissions[15,17].

The FT process is also used as an indirect route for GTL processes. This is where syngas is converted to hydrocarbons in the presence of an iron or cobalt catalyst[13]. The preferred catalyst of choice is Cobalt for the low temperature FT (LTFT) process. This is due to its high activity and selectivity towards desired products, including the absence of the WGS reaction. The LTFT process is more commonly used in industry for the synthesis of liquid fuels. A mixture of hydrocarbons is generated from the reaction which can range from CH_4 to hydrocarbons that have over 100 carbon atoms. The low carbon number products must be reduced in order to make the process most effective as they cannot be used as liquid fuels. Once the desired hydrocarbons are obtained, they can be processed to form chemicals such as naphtha and diesel. A schematic of the GTL process involving the FT reaction can be
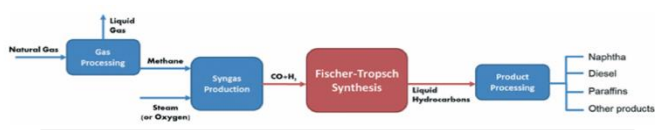

Figure 1: Schematic showing the GTL process involving FT[18]

seen in Fig. 1[18]

2.2 Biomass-to-liquid (BTL)

Biomass can typically be categorised into three main categories: (i) vegetable oils such as palm and soybean oil, (ii) carbohydrates for example, starch and sugars and (iii) lignocellulose solid materials derived from wood[15]. Biofuels produced from these feedstocks can be classified into first, second and third generation biofuels. First generation biofuels, such as bioethanol, can be produced from carbohydrates that

contain sugars and are fermented into ethanol using enzymes that are generated from yeast[19]. Biodiesel is also another common, first generation biofuel, most commonly produced from the biomass feedstock of vegetable oils. It is a desirable renewable fuel due to its biodegradability and low toxic greenhouse gas emissions. It can be produced by the transesterification of vegetable oils with short-chain alcohols. Biodiesel can be used purely as a fuel, or it can be merged with petroleum-based diesel fuel[20-22].

Second generation biofuels are derived from the lignocellulosic solid materials which are obtained from wood and can be produced by two routes; thermochemical and biochemical processing. Thermochemical processing uses heat with varying concentrations of oxygen to heat the biomass, and it enables the conversion of all organic components within the biomass into biofuels[21]. On the other hand, biochemical conversion mainly converts polysaccharides. Biochemical conversion processes are mainly based on microbial and enzymatic methods to produce sugars, which can then be converted into liquid fuels and other chemicals. Thermochemical processes comprise of direct combustion, biomass gasification, biomass liquefaction and pyrolysis of biomass. Direct combustion of biomass, in a good ventilated space, is often utilised for domestic stoves and heating which can be a reliable substitute for fossil fuels. The products of the combustion process are carbon dioxide and water, and the sulphur emissions from this reaction tend to be low[20,23]. Biomass gasification comprises of drying the feedstock, pyrolysis and then gasification of the subsequent products. The process takes place in the presence of oxygen, air, steam or carbon dioxide within a reactor known as a gasifier. The gasification process will lower the carbon to hydrogen mass ratio, and as a result the calorific value of the product is enhanced because of the increased hydrogen fraction. The desired products of the process can be power, heat or biofuels as well as syngas. The syngas can then be processed into liquid fuels by the FT synthesis process, methanol synthesis or hydrogen by WGS[24].

Third generation biofuels are derived from marine biomass, such as algae and micro-algae. Algae has been proven to be a valuable resource in producing biofuels, for example biogas and biodiesel. The micro-algae feedstock used to produce biodiesel contains a very high lipid content, and so it is widely accepted that micro-algae are an economically viable method for biodiesel production[25].

2.3 Solid waste to liquid fuels

Plastics wastes contribute to approximately 15-25% volume of municipal waste in Europe. The consumption of plastic as a percentage of the total waste has increased from less than 1% in 1960 to 11.7% in 2006, and this is expected to increase more within the next few years. Plastics are a large threat to

the environment due to their non-biodegradability, and fast accumulations rate in solid waste streams[26]. Pyrolysis of plastic waste has been found to be an effective method of waste management, as well as producing high quality fuels that can be used for a wide range of purposes[27]. This lowers the dependency on conventional fossil fuels, and also aids environmental problems associated with landfills and incineration of plastic waste. The process has the advantage of being free from toxins production and has low carbon dioxide and monoxide emissions[8]. Pyrolysis involves the thermal degradation of long chained polymers into smaller molecules using high temperatures in the absence of oxygen. The process typically produces pyrolysis liquid oils, gases and solid residue (char). High quantities of liquid oils of up to 80 wt% at temperatures of approximately 500°C can be attained. The liquid oils generated can be used in furnaces, turbines and diesel engines, with no requirement for treatment or upgrading[28].

Thermal pyrolysis is a non-catalytic process and produces a volatile fraction of gases that can be divided into condensable hydrocarbon oils comprised of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non- condensable high calorific value gas. The pyrolysis process can also take place with the use of catalysts, known as catalytic pyrolysis, which substantially lower the pyrolysis temperatures and reaction times, and increases the gaseous product yield[8,26].

2.4 Coal-to-liquid (CTL)

Coal can also be used as a basis for the production of alternative liquid fuels through three main routes: (i) pyrolysis; (ii) direct and (iii) indirect coal liquefaction. The pyrolysis process involves conversion of coal to liquid fuels, gases and chars through heating to temperatures greater than 400°C. The char produced is hydrogen deficient which causes gases and liquids rich in hydrogen to be produced. The char produced from this process amounts to approximately 45 wt% of the coal feedstock[29]. As a result, such processes have been deemed uneconomic and inefficient[30]. However, the process can take place with the presence of hydrogen, known as hydro-carbonisation. The composition and yields of the products vary with the process in the absence of hydrogen, but the yields generated depend heavily on the process parameters for example, pressure, residence time, heating rate and type of coal feedstock[29,31].

Direct coal liquefaction involves dissolving coal at very high temperatures and pressures. Hydrocracking then takes place, breaking down long carbon chains into shorter ones in the presence of hydrogen and a catalyst. The addition of hydrogen in this process has been found to improve the H:C ratio of the product. Liquid yields greater than 70% of the dry coal weight can be achieved with overall thermal efficiencies of approximately 60-70%. The liquid fuels produced from this

method are of a higher purity when compared to the fuels obtained from the pyrolysis of coal[31]. The fuel can be readily used in power generation or as synthetic crude oil in other chemical processes. However, further upgrading of the oil is required for subsequent use as transport fuel[30]. The indirect coal liquefaction process consists of two stages. The first stage involves the production of syngas, which is then followed by the second stage where the syngas is converted to liquid fuels using catalytic processes. The syngas can be converted into fuels using the FT process, or it can be converted to chemicals such as methanol and DME[15].

3. Major limitations of current conventional units and reactors

There are a number of reactors that can be used for industrial scale liquid fuel synthesis. These reactors include: multi-tubular fixed bed reactors (i.e. trickle flow reactor), fluidized bed reactors (FBR) (bubbling or circulating fluidized beds)[32] auto-thermal reactors, slurry-bed reactors and entrained flow reactors. Multi-tubular fixed bed reactors contain multiple tubes with small internal diameters; these tubes house catalyst and are submerged in water which is used to reduce the heat produced from the chemical reaction[33-34].

Multi-tubular fixed bed reactors are vulnerable to carbon deposition when exposed to temperatures higher than 530K. Carbon deposition in multi-tubular fixed bed reactors can lead to the blockage of the reactor and its fittings over time. Multi-tubular fixed bed reactors are also subject to high pressure drops that are relatively higher than those in FBR. Hence, these reactors tend to be complex and expensive[35]. In addition, the scale-up of multi-tubular reactors can be mechanically difficult and complicated due to operational and environmental factors. They are also considered to be maintenance and labour intensive[32-35], as the catalysts used in these reactors must be replaced periodically. FBRs are commonly used for high-temperature FT processes, namely for the production of light unsaturated hydrocarbons in the presence of alkalized fused iron catalysts. Slurry phase reactors contains slurry phase derived wax from process with catalysts dispersed in it. The limitation of a slurry-bed reactor is the conversion in a once through systems[34].

The majority of biodiesel is synthesised nowadays by the transesterification of plant oils or animal fats with methanol in the presence of homogeneous base catalysts in stirred tank reactors. The yield would typically reach 96.5%[36-37]. However, due to the immiscibility between alcohols and oils, the reaction rate is often constrained by mass transfer. As a result, it was predicted that a higher yield of biodiesel could be achieved by increasing the mixing intensity. Thus, increasing interaction and consequently the mass transfer of the process. Moreover, the productivity rate of biodiesel was often low

when carried out in batch processes. This has demonstrated lower efficiency of the process as well. Conventional macroscopic reactors have drastically lowered mass and heat transfer coefficients when compared to microreactors for the same process[36]. Another disadvantage is the longer residence time required to produce a high yield of products. For example, Wen et al.[38] found that it takes a microreactor between 14 to 39 seconds to generate a biodiesel yield of 97.3%, as opposed to a batch reactor which requires approximately 1 hour to produce the same yield. If a process is to be scaled up to achieve higher capacities, then it would be extremely difficult with conventional reactors. Increasing the size of these reactors would require the increase in size of each reactor unit. This can make the whole scale up process very expensive, time consuming and labour intensive[39].

4. Advantages of using microreactors for liquid fuel synthesis

Microreactors are typically classified as having a network of channels (typical dimensions between 10-300 μm) usually etched into a solid substrate for example a glass chip[40]. These units offer the opportunity of miniaturizing traditional macroscopic reactors used in the chemical industries. Their main feature is their high yields of fuel produced in short reaction times. Microreactors can be used for many multiphase reactions to produce liquid fuels, and these reactions have been improved by their advantageous properties. Microreactors have been used more commonly in the pharmaceutical and chemical industries. However, the possibility of using them for liquid fuel synthesis is now gaining increasing attention[41], with the most prominent advantages highlighted below.

4.1 Enhanced surface-area-to-volume-ratio

Microreactors are characterized with large surface area. The volume ratio is typically found in the range of 10,000 and 50,000 m^2m^{-3}, as opposed to conventional macroscopic reactors which often have ratios around 100 m^2 m^{-3}. This creates the desired environment for multiphase reactions to be established on the interfacial area between the different phases[42]. The reduced size of microreactors leads to a lesser amount of reagent required for the process[43].

4.2 Improvement of mass and heat transfer

Due to the high surface area to volume ratio, the mass and heat transfer efficiency is improved[44-45]. A swifter heating and cooling is achieved which provides a higher temperature control in a reaction. Subsequently, heat transfer coefficients are improved to an order of magnitude higher than the ones obtained in regular heat exchangers with values up to 25 kWm^{-2}K^{-1} [46-47]. This is beneficial for both fast exothermic and endothermic catalytic reactions, such as in FT process[46]. The

enhanced surface to volume ratio also leads to microreactors exhibiting efficient input and removal of heat. Therefore, it enables achieving constant isothermal conditions. Furthermore, it is also possible to control the mass transfer in a microchannels for a specific chemical process using varying geometries and different flow rates[48].

4.3 Shorter residence time

The residence time can be significantly reduced by shortening the length of the microchannels. Thus, reactions which contain unstable reactive intermediates can be better controlled due to this specific attribute[49]. The biodiesel synthesis process is an example of this, where a residence time of 28 seconds is required to achieve a biodiesel yield of 97.3% in a microreactor. The same is achieved in a batch reactor after 1 hour. As opposed to a batch reactor requiring 1 hour to achieve the same yield[38].

The enhanced area to volume ratio, together with the reduced residence time and the enhanced mass and heat transfer efficiency lead to significantly reduced reaction times for the process. As a result, using microreactors to produce liquid fuels in some cases can generate excellent yields in under 1 minute[38].

4.4 Greener operation and sustainability

As the mass and heat transfer are improved, product selectivity will be higher and thus resulting in lesser produced waste. The residence time in microreactors enables many of the reactions to function under milder conditions (e.g. lower temperatures and pressures). This significantly decreases the energy required for cooling exothermic reactions like the FT process, as well as, the need for auxiliary substances. Moreover, using microreactors allows on-demand and on-site synthesis resulting in less energy required for transportation and easier more convenient recycling of the substances[43]. Using solvents for the purification of products is a heavy contributor to waste in a chemical process. Microreactors can provide solvent free purification which reduces the amount of waste generated[50].

4.5 Numbering up

These reactors have the potential to be scaled up[51]. Microreactors of similar dimensions can be connected to functions in series or parallel, referred to as numbering up. In doing so, production capacities can be enhanced much more efficiently than conventional reactor setups which would require the resizing of each individual reactor unit. Therefore, scaling up is more convenient and less time consuming. Moreover, the plant operation can remain continuous and undisturbed even if a malfunction occurs in one of the microreactors, as the remaining units will continue to operate either in parallel or series[39]. Deshmukh et al.[52] evaluated the scalability of microchannel reactors used for the FT process. The results showed that each reactor exhibited equal

performance in terms of CO conversion and selectivity profile to various hydrocarbons. This indicates that the scalability of these microreactors has been proven to be successful. The robustness of the catalyst and microreactor system was tested through a long experimental run with >4000 hours of operation and numerous regeneration cycles. The results concluded that flexibility is possible when designing a flow sheet for an industrial plant. Hence, implementing microreactors allows for process intensification and size reduction within a chemical plant[52-53].

4.6 Offshore fuel production

Microreactors can be developed to allow offshore production of methanol from natural gas. Although offshore regions contain an abundant supply of natural gas (e.g. methane), delivering this to the market place is linked with numerous logistical challenges and costs. To overcome this problem, an effective solution would be the conversion of CH_4 gas to liquid fuel using microreactors. CH_4 can be converted into methanol on an offshore floating production, storage and offloading (FPSO) vessel. Conventional reactors used for the liquid fuel synthesis from natural gas would not be suitable to the conditions of the floating vessel. This is due to the vessels being extremely space and weight controlled which can adversely affect the stability of the vessel during extreme weather conditions. However, microreactors, as shown by Tonkovich et al.[54] would be a novel alternative. In their work, multiple microreactors for phase separation and distillation for product purification to form a microchannel-based unit, was configured into a novel system. The results showed that it is possible to integrate microreactor technology to be used on a FPSO for methanol synthesis. and distillation and separation processes, in otherwise difficult to access locations.

5. Microreactors for liquid fuel synthesis

Microreactors have been extensively used over the past two decades to produce fuels derived from biomass, utilized in FT process and from natural gas to produce methanol. The most common types are the micro-tubular, the multi-microchannel, the packed bed, and the slug flow microreactors, together with the coated wall as well as the microplasma reactors. Table 1 shows a summary of the microreactors used for the different liquid fuel production routes.

Type of microreactor	Type of catalysts	Fuel produced
Micro-tubular reactor	Homogeneous	Biodiesel
Multi-microchannel reactor	Homogeneous	Biodiesel
- **T shaped microchannel**		
- **Serpentine microchannel**		
- **Zigzag microchannel**		
Packed bed microreactor	Heterogeneous	Biodiesel
		FT fuel
		Methanol
Slug flow microreactor	Heterogeneous	FT fuel
Coated wall microreactor	Heterogeneous	FT fuel
Microplasma reactor	No catalyst	Methanol

Table 1: Microreactors used for liquid fuel

Micro-tubular reactors and multi-microchannel reactors are most commonly used to synthesise biodiesel using a homogeneous alkali catalyst. The packed bed microreactor consists of the catalyst loaded directly inside the reactor, whereas the slug flow microreactor uses structured catalysts to generate a slug flow pattern. The coated wall microreactor is similar to the slug flow one. However, there are differences in the way in which heat is removed and the flow patterns generated. These specific reactors make use of heterogeneous catalysis for, predominantly, the FT process52. Microplasma reactors allow the direct partial oxidation of CH4 gas into methanol at milder reaction conditions. The microreactors essentially consist of a quartz tube with a metal wire inside in which a high voltage is then applied to generate the microplasma. Studies have shown that it is possible to replicate a highly reactive environment at lower temperatures inside the microreactor which is highly sustainable and flexible[55].

5.1 Micro-tubular reactors

These reactors have been more commonly used to enhance the efficiency of the homogeneously alkali-catalysed biodiesel production process[56-58]. The alkali catalysts used for the process are NaOH or KOH. The catalysts are subsequently mixed well with the reactants and fed into the microreactor to generate the reaction. Homogeneous catalysis has several advantages over heterogeneous ones, namely the advantages of enhanced activity and selectivity[59]. Azam et al.[60] used a micro-tubular reactor (see Fig. 2(a)) with KOH catalyst to produce biodiesel from the transesterification of palm oil, and the microreactor was subsequently compared with a milli-channel reactor (inner tube diameters 0.58 and 1.6 mm respectively). The results showed that a higher conversion (>95%) was achieved in the micro-tubular reactor with the KOH catalyst at a shorter residence time of 180 seconds. This shows that microreactors have the ability to reach higher biodiesel yields at smaller reaction times.

Sun et al.[61] also carried out KOH-catalysed synthesis of biodiesel in micro-tubular reactors, with raw materials used for the process being unrefined rapeseed and cottonseed oils. Two different microreactors were used for biodiesel synthesis. The first one was made out of a stainless-steel capillary with an inner diameter of 0.25 mm or 2 mm and length of 30 m. The second microreactor consisted of a quartz tube with an inner diameter of 0.25 mm or 0.53 mm and length of 30 m. The results obtained from the reaction showed that a methyl ester yield greater than 95% can be achieved in these microreactors at residence times of less than 10 minutes. It was also found that the methyl ester yield increases with increasing KOH concentration; however, when

the KOH concentration reaches a certain point (1% conversion), the methyl ester yield starts to decrease. López-Guajardo et al.[62] used a micro-tubular reactor to produce biodiesel from sunflower oil using the catalyst NaOH. The microreactor was made out of stainless steel and had an internal diameter of 0.71 mm and a 5 m length. The results showed that the microreactor was able to achieve higher yields of biodiesel at very short residence times- 99% conversion in 4 minutes, as opposed to a conventional batch reactor which reaches a yield of 99% in 60 minutes - a factor of 15 longer than the micro-tubular reactor.

5.2 Multi-microchannel reactors

To further enhance the biodiesel production process in microreactors, multi-microchannel reactors have also been developed to produce high yields in shorter reaction times[38,63]. These microreactors consist of numerous microchannels etched on glass or polymer materials to synthesize liquid fuels. Multi-microchannel reactors can generate higher fuel yields in shorter residence times as the larger number of channels increases the reaction surface area. If these channels are further folded into a serpentine shape, the surface area will increase. Santana et al.[63] used a T-shaped microreactor to produce biodiesel from sunflower oil using NaOH as a catalyst (Fig. 2(b)). The microreactor had a width of 1.5 mm, a height of 0.2 mm, a longitudinal length of 411 mm and was made of polydimetilsiloxane. The microchannel reactor was constructed by first choosing the solid substrate and then photographing the microchannels on a photosensitive polymer, reproducing the microfluidic devices and sealing them. The results showed that the microreactor achieved a biodiesel conversion of 95.8% at a reaction time of 1 minute, as opposed to a conventional batch reactor, which achieves a conversion of 94.1% at 180 minutes. The shortened length of the microreactor enhances the mass and heat transfer rates leading to shorter reaction times. It was also demonstrated that biodiesel production process improves dramatically by implementing a micromixer with static elements within the reactor (see Fig. 2(c)). It was previously noted that biodiesel conversion of 99.53% was achieved at a residence time of approximately 12 seconds and a reaction temperature of 50°C[64]. This indicates that that the implementation of micromixers with static elements can significantly/dramatically improve the biodiesel synthesis process.

Bhoi et al.[65] studied the synthesis of biodiesel from sunflower oil using KOH catalyst in three multi-microchannel reactors which consisted of a serpentine microchannel etched in a glass chip but varied in microfluidic junctions i.e. dispersion devices (see Fig. 2(d)). The results showed that all three types of reactors generated conversions greater than 90% with residence times of 1-2 minutes. It was concluded that any of the three microreactors provide excellent biodiesel yields. Wen et al.[38] developed a zigzag microchannel reactor to

produce biodiesel from soybean oil catalysed by alkali solution as depicted in Fig, 2(e). It was constructed from stainless steel by electric spark processing. The reactor consists of three types of patterned sheets: (i) the middle sheet had a zigzag microchannel on it; (ii) the cover sheet consisted of two holes performing as flow paths, and (iii) the bottom sheet acted as a support for the microreactor. The microchannels are rectangular with a length of 1.07 m. The results showed that the reaction has a very high efficiency due to the incredibly small residence time of 28 seconds and produces a methyl ester yield of 99.5%. Moreover, it was found that the reaction could function at a milder temperature of 56°C. These studies showed that the geometry of the multi-microchannel reactors can have great influences on the product yield achieved, with the zigzag or serpentine shape geometries increasing the surface area and hence reducing reaction times, whilst still achieving high yields (> 90%).
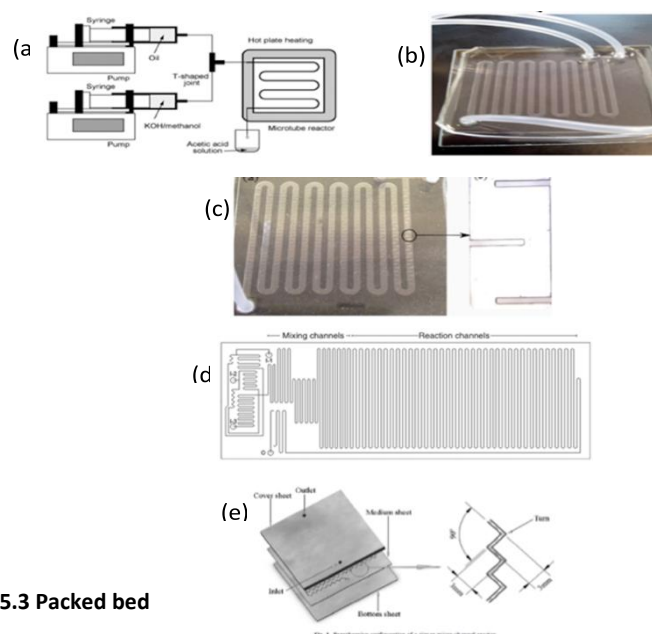
5.3 Packed bed

Figure 2: Types of micro-tubular and multi-microchannel reactors used for biofuel synthesis: (a) schematic diagram of the microtube reactor system[60]; (b) T-Shaped Microreactor[63]; (c) Microreactor based on micromixer with static elements[64]; (d) Schematic diagram of the serpentine microchannel etched in glass chip[65]; (e) Representation of zigzag microchannel reactor used for biodiesel synthesis[38]

microreactors

The main advantages of using a packed bed microreactor is the ability to load and replace catalysts easily, and the ability to use spent catalysts as a more sustainable practice[60, 66-67]. Traditionally, in packed bed reactors, the catalyst is loaded into the packed bed directly. Although using homogeneous catalysis has its advantages, there are often problems regarding separation of the catalyst from the product especially in large-scale processes[59]. Using heterogeneous catalysis can overcome this because it allows simpler more economical separation processes, and a reduced water load

which allows for a more environmentally sustainable process[68]. Chueluecha et al.[69] continuously synthesised biodiesel in a packed bed microreactor (dimensions 60×1×0.5mm) using a heterogeneous catalyst (CaO) as shown in Fig. 3(a). The catalyst was activated with methanol to improve the catalytic performance for the transesterification reaction of refined palm oil. A biodiesel purity of 99% was achieved with a residence time of 8.9 minutes and a reaction temperature of 65°C. Therefore, a high fuel quality and superior productivity performance can be achieved from the packed bed microreactor. Furthermore, Chueluecha et al.[70] carried out further research to enhance biodiesel synthesis using the same heterogeneous catalyst, but this time using a co-solvent (iso-propanol) in a packed bed microreactor. The results showed that the biodiesel production process significantly improved due to the shorter residence time required. This time the optimum conditions required were a residence time of 6.5 minutes which provided a product purity of 99%. Therefore, using a co-solvent enhances the synthesis of biodiesel in a packed microchannel reactor by reducing the residence time of the reaction and reducing the amount of required methanol reagent. Biodiesel synthesis can take place using enzymatic catalysts (biocatalysts) in packed bed microreactors. Such biocatalysts, for example lipase, are hydrolytic enzymes which have the ability to catalyse hydrolysis, esterification and transesterification. They can catalyse these reactions under milder process conditions, they can be reused, the separation required during the process is easier and the process is more environmentally friendly. This makes the process more sustainable on an industrial scale[41].

The packed bed microreactor is a type of microreactors that can be used for the FT process. These reactors can retain the high mass and heat transfer coefficients while significantly improving the catalyst mass to reactor volume ratio within the microreactor[60]. Myrstad et al.[71] designed and manufactured a packed bed microreactor (Fig. 3(b)) and studied its performance using heterogeneous high activity cobalt/alumina catalysts. The microreactor used had a volume of 2 cm^3. The results showed that such microreactors can operate at severe conditions, for example high temperatures, pressures and CO conversion, all while avoiding large temperature gradients and increased catalyst deactivation. Cao et al.[72] designed a packed bed microreactor (Fig. 3(c)) to use for the FT process using Co/Re/Al$_2$O$_3$ catalysts. The reactor system had active cooling to ensure isothermal conditions within the catalyst bed. T reactor also had an in built preheating zone with catalyst bed temperature measurement abilities. It is imperative to ensure that temperature is controlled to minimise the production of CH$_4$ (as this is a highly exothermic reaction), and to increase the catalyst lifespan. It was found that the FT process could operate at a maximum gas hourly space velocity of 60,000 h^{-1} and provides productivity as high as 2.14g C$_{2+}$/(g-cat h) while

still retaining a relatively low methane selectivity and high chain growth probability.

Venvik and Yang[73] developed integrated micro packed-bed reactor/heat exchangers (Fig.3(d)) for methanol fuel synthesis. The addition of the integrated heat exchanger was desirable as it removed excess allowing methanol synthesis under extreme conditions, without hot spot formation and excessive catalyst deactivation. Furthermore, this particular microreactor can be established as an isothermal/ isobaric reaction environment devoid of internal or external mass transfer limitations. As a result, different catalysts can be used to accomplish high volumetric and gravimetric productivity. However, carrying out liquid-gas reactions can also be problematic if the gases involved are toxic or corrosive. In this case, microreactors have to be specifically designed to allow the precise control of gas inflow and the contact time between the gas and liquid must be carefully monitored. To minimise the problem, integrated gas-liquid separators can be implemented to distinguish the gaseous phase at the end of the chemical reaction[74]. Bakhtiary-Davijany et al.[75-76], devised and tested a multi-slit Integrated Micro Packed Bed Reactor-Heat Exchanger (IMPBRHE) for the production of methanol from synthesis gas over at Cu/ZnO/Al$_2$O$_3$ catalyst under the reaction conditions of 80 bar and 523K (Fig. 3(e)). The performance of the microreactor was compared with that of a laboratory packed-bed reactor. The study found that the IMPBRHE had negligible internal and external mass transfer limitations. The reactor also demonstrated benefits such as isothermal functionality, narrow residence time distribution and low pressure drops as opposed to the conventional packed bed reactor. The notable feature of the microreactor is the higher thermal stability. This is a desirable feature in exothermic reactions as these are often restricted by thermodynamic equilibrium, e.g. the methanol synthesis reaction. Furthermore, the IMPBRHE has the potential to be scaled up to a larger capacity which is not possible in the fixed bed reactor due to the differences in scaling up concept.

Although using a packed bed microreactor has several benefits, these particular reactors are often subject to high pressure drops due to the use of small catalyst pellets. However, it was found that an adequate level of pressure drop can be achieved with substantially small catalyst pellets (100 μm) while retaining a high catalyst effectivity[18]. Using packed bed microreactors has proven to be beneficial for liquid fuel synthesis but they can be subject to plugging or fowling of the channel network due to the use of solid catalyst particles. As a result, the desired continuous flow is obstructed. To overcome this, catalytically active metals can be used to cover the inside walls of the microreactor or can be placed on poles in the reactor channels, as seen in slug flow microreactors and coated wall microreactors[74].

5.4 Slug flow microreactors

Slug flow microreactors contain structured catalysts (e.g. monoliths and foams) (Fig. 4(a)) and they are mainly used for the FT process, as they overcome some of the problems faced with conventional packed bed reactors; a typical problem within conventional packed bed reactors is the disordered nature of the turbulent flow between the catalyst pellets within the packed bed. Slug flow reactors display a laminar flow due to their organized spatial structures within the reactor. As a result, there is an improved control of mass and heat transfer. The structured catalysts used in the FT process are constructed by coating a structured support, i.e. a honeycomb monolith, with a fine layer of the catalyst. In doing so, the catalyst and the reactor are in continuous intimate contact. A monolith coated catalyst essentially consists of an array of parallel microchannels that are separated by thin walls which are coated with the active catalyst. In such designs, the gas bubbles are separated by the liquid phase flow with a fine layer of liquid between the gas bubbles and the walls that are coated with the catalyst. This significantly reduces the distance required for the reactant molecules from the gas phase to travel to the active catalyst site. As a result, mass and heat transport resistance are reduced. The monolith structure has a high open cross-sectional area for the fluid to flow through which generates substantially low pressure drops. Other microstructured catalysts, e.g. foams, wires and fibres have been found to generate similar values for mass and heat transport rates with slightly higher pressure drops, and the flow in these structures is found to be plug flow[18].
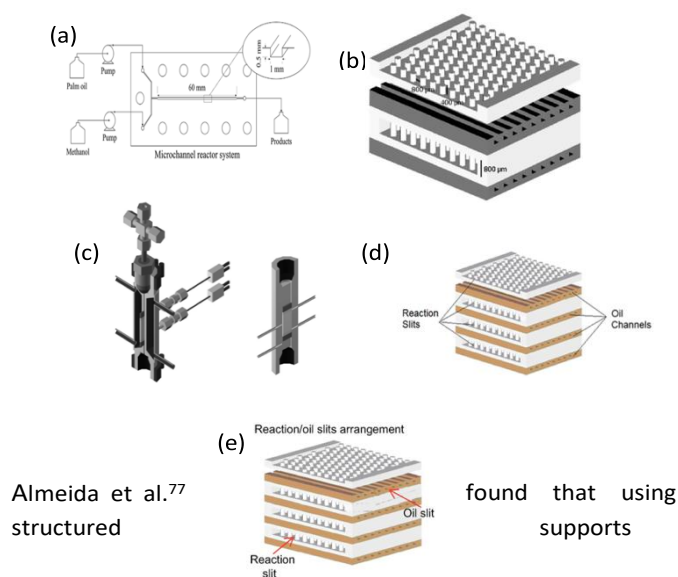
Almeida et al.[77] found that using structured supports

Figure 3: Schematics of different types of packed bed microreactors used for liquid fuel synthesis: (a)packed microchannel reactor[69-70](b) microstructured reactor, showing the pillar structured catalyst foils and the cross-flow rectangular oil channels[71]; (c) microchannel catalytic reactor[72] (d) geometry of the reaction and heat exchange channels[73]; (e) the IMPBRHE showing reaction and cooling oil slits[75-76]

with microreactors is a viable option compared to powder catalysts. Furthermore, the C_{5+} selectivity relies on the type of support used, and the layer of thickness of the catalyst amount deposited. It was found that increasing the layer of catalyst loading from 255 to 908 mg, the methane gas selectivity increased from 20.8 to 27.1% for the monolith support, despite the overall CO conversion increasing from 19.2 to 58.2%. De Deugd et al.[78] used the Krishna and Sie method for selecting a multiphase reactor and found the monolith reactor to be best suited for the FT process. However, when using slug flow reactors for the FT process, these reactors often have a low catalyst mass to reactor volume ratio- a small amount of active catalyst is held per reactor volume. This can limit the productivity of the process. An approach to overcome this is to use carbon nanofibres as a support for the FT process, thus improving the activity per reactor volume. However, the catalysts used were subject to fast deactivation in the FT process[18]. There are often concerns surrounding the development of microreactor technology that relates to the cost of the microreactors, and also in finding ways to replace spent catalysts. In order to design a catalytic microreactor precisely, the reactor and the catalyst must be produced simultaneously and must take into account the transport phenomena and intrinsic reaction kinetics[53].

5.5 Coated wall microreactors

Another type of reactor used in the FT process is the coated wall microreactors (Fig. 4(b)). The design of these reactors is similar to the slug flow microreactor; however, the main differences related to the heat removal and flow generation. These reactors can have one or numerous parallel rectangular channels, with the walls coated with a slim layer of the active catalyst. The channels are often arranged into blocks, and they offer excellent mass and heat transfer coefficients because of the high surface area to volume ratio. Therefore, the activity and selectivity are greatly improved. Due to the increase in mass and heat transfer properties, the FT process can now function in extreme process conditions which may be required to achieve the optimum activity and selectivity. Some of these conditions may be higher temperatures and pressures. The type of fluid flow found in these particular reactors is typically laminar, as opposed to the slug flow microreactor[18].

Guettal and Turek[79] carried out a study to compare traditional slurry bubble column and fixed bed reactors with coated wall microreactors and reactors with monolith coated catalysts. Mathematical modelling was carried out as a basis for the work. The results focused on the influence of catalytic activity and the effect of mass and heat transfer on reactor efficiency. The results showed that the slurry bubble column reactor had much better mass and heat transfer characteristics when compared to the fixed bed reactor. The slurry bubble column reactor also needed a smaller mass of the active catalyst and reactor volume. The monolith coated catalyst reactor

performed similarly to the fixed bed reactor in terms of yield and had no problems with heat transfer. Nonetheless, the three reactors investigated in the modelling studies of Guettal and Turek[79] are subject to some practical problems summarised as: (i) elevated flow rate for the liquid recycle required in reactors with monolith coated catalyst, and (ii) removal of catalyst particles from liquid products in the slurry bubble column reactors. However, the coated wall microreactor demonstrated the highest productivity per unit of catalyst volume. It also generated the highest yield without suffering from any of the issues that the other reactors faced. This is due to negligible mass and heat transfer resistances.

Almeida et al.[80] compared the performance of coated wall microreactors with slug flow microreactors encompassing structured catalysts (monolith, foam and micromonolith) and powdered catalysts. The results showed that the coated wall microreactors demonstrated a higher performance compared to the slug flow microreactor. The performance was better in terms of C_{5+} selectivity under similar reaction conditions. Almeida et al.[77] adapted a catalytic test unit for testing a coated wall microreactor during the FT process. The reactor had good temperature and pressure control because the unit was prepared with a cooling line with pressurised water to avoid boiling at the reaction temperature. This particular microreactor showed a high selectivity for C_{5+} which can be acquired during the FT process due to the high degree of temperature control of the microreactor. It was also found that thicker catalyst coating of the microchannel walls can adversely affect the selectivity.

Using coated wall microreactors can reach roughly 10 times higher catalyst productivity, which is defined as kghr^{-1} of synthesis gas per m^3 of catalyst volume. Therefore, capital and operating costs are greatly reduced. When combined with highly active and stable catalysts, coated wall microreactors can achieve excellent volume based productivity, with conversions up to 90% with no thermal runaway or substantial deactivation of the catalysts[73]. Another advantage of having abundant rectangular channels arranged in parallel is that the reactor components can be added or removed to match the production requirements. The components of the reactor are small which enables construction of the reactors required for the FT process in indoor shops, thus speeding up installation. Furthermore, if individual components are needed to be replaced, these can be removed without compromising the facility's overall production rate[54].

Despite all the advantages, there is one notable disadvantage of both the coated wall microreactor and the slug flow microreactor: being the low catalyst mass to reactor volume. This can result in a low fuel yield. In addition, there are often difficulties faced with the procedures required to coat the reactor wall and the necessity for particularly designed catalysts for coating. Replacing spent catalysts with new ones can also be difficult and time consuming[18]. Therefore, a compromise must be made between the type of catalysts and the type of microreactor used to produce a liquid fuel with high yields and short reaction times.
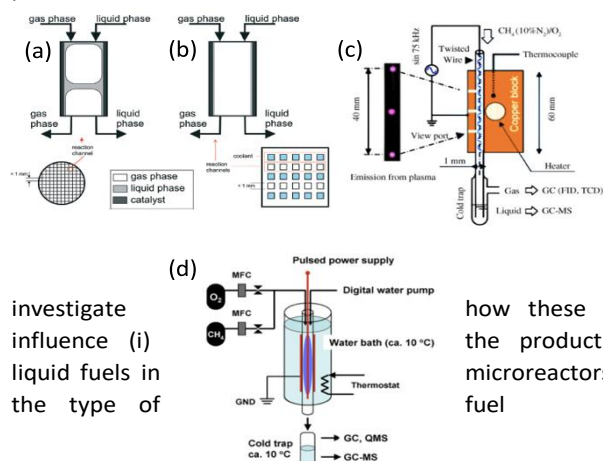
5.6   Microplasma reactors

The partial oxidation of methane to produce methanol directly is an attractive process as the global demand for energy is increasing. It is a way of significantly reducing capital and operating costs. Current processes require a significant amount of toxic chemicals, for example H_2SO_4, and also have long reaction times (2.5 hours), with considerably low yields of methanol. Such processes would normally require elevated temperatures and high demand of energy. These processes are also considered complex due to multistep processes involved in synthesising the produced gas. One way to acquire higher methanol yields is to establish extreme conditions within a single reactor, with temperatures and pressures of 450-500°C and 3-6 MPa, respectively. To the contrary, microplasma reactors can offer the opportunity to achieve this highly reactive environment under much lower temperatures and pressures.

Nozaki et al.[81] developed a microreactor for the partial oxidation of methane in the absence of a catalyst (Fig. 4(c)). The reactor is secured in a heat reservoir (to ensure isothermal conditions), and consisted of glass tube with a metal wire twisted inside. A sine wave of 2 kV at 75 kHz is applied between the metal wire and the heat reservoir. The results showed that single-pass methanol yield of 10% could be achieved at 25°C and 100 kPa. The microreactor faced the problem of plugging in the glass tube by the liquid oxygenates that condensed quickly, which led to an unstable flow. In order to overcome the problems faced and to further improve the yield of methanol, a continuation of the study performed by Nozaki et al.[82] was carried out. They used a non-thermal discharge microreactor (Fig. 4(d)). This was done so that the direct and selective synthesis of organic oxygenates such as methanol, formaldehyde and formic acid were carried out via the partial oxidation of methane at room temperature. The reactor was kept at 10°C which allowed the condensation of the liquid components, whilst separating the products from the oxygen rich plasma. The one pass CH_4 conversion was 40% while the selectivity of the useful oxygenates was 30%-50%. This microreactor produced significantly large amount of syngas with a selectivity of 40%. Moreover, it is also possible to achieve an overall liquid yield of 30% with 80% selectivity. Therefore, using this type of microreactor to produce methanol is an efficient and economical process.

6. Factors influencing liquid fuel synthesis in microreactors

The factors that typically affect the process of liquid fuel synthesis in a microreactor include heat and mass transfer, residence time, microreactor geometry, temperature and pressure. Extensive research has been carried out to

investigate how these factors influence (i) the production of liquid fuels in microreactors; (ii) the type of fuel being

Figure 4: Schematic illustrations showing slug flow, coated wall and microplasma microreactors used for liquid fuel synthesis: a) Slug flow microreactor[18]; b) Coated Wall Microreactor[18]; c) Schematic of the microplasma reactor experimental set up[81]; d) Schematic diagram of microplasma reactor and experimental setup[82]

manufactured; and (iii) the type of catalyst used. It is important to consider the limitations of the microreactor system being used to synthesis liquid fuel and to understand all the governing parameters of the process in relation to the feedstock being used, and the microreactor boundary conditions.

6.1 Heat and mass transfer

Microreactors have higher mass and heat transfer rates compared to conventional reactor units. Consequently, chemical reactions can be conducted under extreme operating conditions of temperature and pressure to achieve higher yields. Günther and Jensen[83] reported that the large interfacial areas that are related with microscale flows allow enhanced mass transfer between two immiscible fluids. Segmented flows generated inside microreactors enable more efficient mixing and reduce dispersion in the flow direction. Microreactors can achieve rapid reaction rates by exploiting their high surface area per volume ratios. Hence, the efficiency of heat transfer is

improved significantly[68,84]. The enhanced heat transfer is beneficial to any chemical process. The overall heat transfer coefficient for microchannel heat exchangers and microreactors are found to be greater than 20 kW/(m²K). This is in contrast to overall heat transfer coefficients of less than 2 kW/(m²K), which are found in conventional bulk reactors[85].

Wen at al.[38] reported that methyl ester yield in biodiesel production is strongly dependent on the droplet size. They found that the reactor which generated the smallest droplet, showed the highest activity. This demonstrated the optimum performance during biodiesel synthesis due to enhanced mass transfer. Furthermore, methanolysis reaction is a heterogeneous and one. It is well acknowledged that the amalgamations of varying physical and chemical processes will affect the kinetics. It has been reported that mass transfer of triglycerides from the oil phase towards the methanol/oil interface can limit the methanolysis reaction and control the kinetics at the beginning of the reaction[86]. The overall volumetric mass transfer coefficient of triglycerides will increase due to the increase of the specific interfacial area by reducing the size of the droplets, and as a result, the rate of reaction for triglycerides will increase. Therefore, the methyl ester yield is heavily reliant on the droplet size[86].

Microreactors have substantially smaller volumes and still retain an enhanced productivity. The highly improved mass transfer in microreactors when compared to conventional macroscopic reactors, is mainly due to the high gas-liquid phase interfacial area. In microreactors, the two phases are required to mix over the catalyst in a controlled volume relative to the standard pellet size length. Commonly, trickle bed reactor catalyst pellets have dimensions between 4-8 mm as opposed to the microreactor catalyst pellets which have a size of 50 μm. This represents approximately a 100 fold increase in the surface area to volume ratio. As a result, mass transfer in microreactors is significantly enhanced. Such small catalyst particles cannot be used in a standard laboratory reactor as non-uniform flow distributions would be generated, as well as very high pressure drops[89]. Furthermore, the liquid phase volumetric mass transfer coefficient in microreactors is typically one to two times larger than those of large conventional multiphase reactors. Again, this is typically due to an enhanced specific interfacial area found in microreactors. The typical values of the liquid-phase and gas-phase mass transfer coefficients in falling film microreactors are in the ranges of 1×10^{-6} to 1×10^{-5} ms^{-1}, and 10^3 and 10^{-2} ms^{-1} respectively[90].

Tadepalli et al.[44] studied and compared the performance of a packed bed microreactor and a semi-batch reactor for the catalytic hydrogenation of o-nitroanisole (a component of pyrolysis oil). The semi-batch reactor used for this study had a capacity of 25 ml while the packed-bed microreactor had an

internal diameter of 775 μm. The performance of both reactors was evaluated to determine the reactor system best suited for studying hydrogenation reaction kinetics. It was noted that although the reaction rates for both reactors were similar under similar conditions, the mass transfer coefficient of the microreactor was two orders of magnitude higher than in the semi-batch reactor. The advantage of having higher mass transfer coefficients in the microreactors facilitates the process of obtaining intrinsic kinetic data, especially for fast hydrogenation reactions[87].

6.2 Residence time

Residence time is a main parameter that can affect liquid fuel synthesis in microreactors. The residence time varies considerably with the type and configuration of the reactor. The main advantage of microchannel reactors is that fact that residence times are on an average of 10 to 100 times shorter than in conventional batch reactors[68, 90-91]. Moreover, it has been reported by Canter et al.[91] that it is possible to synthesise biodiesel in a microreactor of a size of a conventional credit card, with a residence time of 4 minutes. This microreactor can still yield above 90% of product. Azam et al.[60] investigated the production of biodiesel in micro-tubular reactors with results showing that the conversion increased significantly with increasing residence time. Longer residence times are required for the completed transesterification reaction. However, the excellent mixing in the micro-tubular reactors allows these residence times to still be much shorter than those that would have been witnessed in conventional reactors.

Santacesaria et al.[92] used a micro-tubular reactor to produce biodiesel. They found that as the residence time of the reaction increases, so does the yield of methyl esters. However, this only occurs until a maximum is reached, and further increasing the residence time beyond this point will result in a decrease of the yield. The lowest value of the yield observed at the maximum residence time may be due to a less active micromixing, which leads to the reduction of the interfacial area. The lowest value of the yield at the smaller residence time seems like the typical behaviour of a chemical reaction system (shorter the residence times the lower the yield). Furthermore, for a microchannel which has a fixed length, a longer residence time corresponds to a lower average velocity and the smaller capillary number of Ca which is undesirable for the formation of smaller droplets. As a result, the overall volumetric mass transfer coefficient is deteriorated. This then causes a decrease in the methyl ester yield. However, increasing the residence time has proven to be favourable for biodiesel synthesis[88].

Chueluecha et al.[69-70], carried out biodiesel synthesis in a packed bed microreactor using the residence time range of 0.9 to 11.8 minutes. They found that the conversion significantly increased from 2.5 to 77.5%, as the reaction time increased from 0.9 to 4.4 minutes. Furthermore, Sun et al.[93] also found that prolonging the residence time would increase the yield of biodiesel in the microstructured reactor. However, increasing the residence time too much can have an adverse effect on the biodiesel yield. This is because, increasing it up to a certain point may result in the backward reaction, causing the formation of reactants from products[36].

The effect of residence time has also been tested in microreactors used for the FT process. Almeida et al.[77] tested the influence of residence time on FT synthesis in microchannel reactors. The residence time within the reactors were controlled by varying the flowrate of syngas. The other operating conditions remained unchanged with a pressure and temperature of 10 bar and 523K, respectively. Results from this study showed that CO conversion also increases with an increase in residence time (decreasing the flowrate). It was also reported that the selectivity of C_{5+} products decreased with an increase in residence time.

6.3 Reactor geometry

As many previous studies have shown, the geometry of a micro-reactor has a direct effect on the production yield of the liquid fuel. Günther and Jensen[83] have stated that the layout and size of the reactor have major influences on the reaction. Different geometric parameters inside the microreactor can affect the flow type and droplet size. Microreactors which generate the smallest droplets will have an increased interfacial area which in turn increases the mass transfer coefficient. Therefore, the rate of reaction is affected. Azam et al.[60] found that the highest conversion of biodiesel was achieved in microtubular reactors with the smallest internal diameter. This is because the smaller tubes achieve the highest interfacial area resulting in higher mass and heat transfer. Therefore, the internal diameter of the microtube reactor can potentially have a significant effect on biodiesel conversion. Sun et al.[61] also found that the dimensions of the microreactors have a significant effect on the biodiesel production process. The quartz micro-tubular reactor (inner diameter of 0.53 mm) achieved a methyl ester conversion of 96.7% with a residence time of 8.2 minutes, as opposed to the quartz capillary microreactor (inner diameter of 0.25 mm) which achieved a methyl ester yield of 98.8% at a residence time of 6 minutes. As the inner diameter of the capillary microreactor decreases, the methyl ester yield increased due to the enhanced specific surface area. Subsequently, an increase of mass transfer was noted. The smaller size microreactor also benefited from smaller residence times. In addition, Sun et al.[93] reported in another study that increasing efficiencies was noted when multi-lamination micro-mixers are utilised. This is mainly due to the size of the droplets that are generated which increase the contact area between methanol and oil for biodiesel synthesis.

Furthermore, Santacesaria et al.[94] tested three micro-tubular reactors for biodiesel synthesis which differed in the size of spheres used as packing inside the micro-tubes. The three microreactors gave rise to micro-channels with size of 1000 μm, 500 μm and 300 μm, respectively. The results showed that the smallest microchannel reactor (e.g. 300mm) produced the highest yields compared to the other two reactors (i.e. 500 mm, and 1000 mm) for the same residence time. This can be accredited to the formation of a larger surface area at the liquid-liquid interface Therefore, narrower micro-channels generate higher product yields at shorter residence times. Wen et al.[38] went a step further in terms of geometry layouts, and studied the effect of a zigzag geometry within the multi-microchannel reactor for the synthesis of biodiesel. The results showed that the biodiesel yield increases with the increase of the periodic turn numbers. The effect of the size of the hydraulic diameter was also investigated, and the results showed that as the size of the hydraulic diameter decreases, the biodiesel yield increases. For example, the yield of biodiesel increased from 71.0% to 97.3% with hydraulic diameters of 900 μm to 240 μm, respectively. Furthermore, the reactor which generates the smallest droplets showed the highest activity This demonstrates the optimal performance for biodiesel production. Therefore, it can be noted that reactors with the smallest channel diameter and the most turns are the most favourable for biodiesel synthesis.

Almeida et al.[77], tested different metallic supports which were aluminium foams of 40ppi, honeycomb monolith and micro monolith of 350 and 1180 cpsi, respectively. These were loaded with a Co and Re catalyst using Al_2O_3 as a support whilst varying the thickness. These catalyst supports were then compared to a coated wall microchannel reactor which had perpendicular channels for heating and cooling containing the same catalyst. The results showed that the coated wall microchannel reactor had the highest C_{5+} selectivity compared to any of the other structures. This is due to the better temperature control within the microreactor. The thickness of catalyst coating on the structured supports also affected the C_{5+} selectivity. Therefore, controlling the catalyst loading thickness and reactor geometry can enable an efficient microreactor design for the FT process.

6.4 Temperature

Increasing the temperature of the biodiesel synthesis reaction to some extent, can increase the rate of reaction and enhance the fuel yield. Once the reaction reaches the optimum temperature at which the maximum yield can be obtained, the yield will start to decrease for temperatures higher than the optimal temperature. Santana et al.[64] performed biodiesel synthesis in micromixers with static elements and found that increasing the temperature from 25°C to 75°C increases the biodiesel conversion from 34.32% to 91.53%. This positive relationship can be attributed to the increase of the oil-ethanol miscibility, which subsequently can improve the contact area and mass transfer rates. However, increasing the temperature past 75°C will start to decrease the conversion of biodiesel. This could be due to the evaporation of alcohol which reduces the amount of alcohol reagent available. The decrease in yield with temperature may also be due to the flow pattern changing from slug to bubble flow. Chueluecha et al.[69-70], investigated the effect of temperature on biodiesel synthesis using a reaction temperature range of 50-70°C. It was found that the rate of reaction was strongly influenced by the temperature, resulting in increased conversions with higher temperatures. These findings are consistent with Arrhenius' law which states that the reaction rate constant is a function of temperature. Increasing the reaction temperature will display beneficial physical effects in the system such as enhanced miscibility for methanol and oil. Xie et al.[68], found that the product yield for fatty acid methyl ester increased from 96% to over 99% when the temperature of the microreactor increased from 30°C to 60°C. On the other hand, there was a slight decrease in the product yield after additional increase in temperature to 70°C. Although there was a slight increase in yield of product, it was found that the reaction could function at lower temperatures, and that increasing the temperature above the optimal value would have a minimal effect on the methyl ester production compared to changes in residence time and reactor geometry. Although the shorter residence times required in microreactors is desirable, the residence times must be carefully controlled to prevent the saponification of biodiesel with the KOH.

The FT process typically operates between reaction temperatures of 200-350°C, and pressures within the range of 20-30 bar. The process is highly exothermic and the product distribution is sensitive to operational conditions. Moreover, inadequate heat transfer during the FT process can result in high temperature gradients and local hot spots. This can result in metal sintering and a higher rate of catalytic deactivation. Therefore, proper heat transfer is required to minimise heat gradients and to maximise the product yield. On the other hand, to maintain the catalyst stability; both the heat exchange and temperature must be controlled with high precision. Using a packed bed microreactor for this process, allows an equivalent conversion and selectivity to be achieved at 20K lower reaction temperatures, when compared to a conventional fixed bed reactor[93]. Microreactors have the ability to provide excellent heat transfer from the catalyst bed to the heat transfer oil[71]. Microchannel reactors were tested and proved efficient for FT processing[77]. The FT process can be generally used for the indirect conversion of coal, biomass and gas to fuels. The temperature for the experiments varied systematically between 493K and 523K with the results showing a positive correlation between temperature increase and CO conversion i.e. an increase in the operating

temperature leading to an increase in CO conversion and selectivity of lighter hydrocarbons.

6.5 Pressure

Although smaller microchannel sizes are known to generate the highest fuel yields, the pressure drop in these particular reactors increases substantially with a decrease in the microchannel size. As a result, there is an increased difficulty in operating and production costs. One effectual solution to this problem would be to insert what are known as Dixon rings into a large tube, which lower the pressure drops, and subsequently generate a high fuel yield in a smaller time[94]. Wen et al.[38] found that although smaller hydraulic diameters and more turns within the zigzag microreactor are beneficial, the corresponding pressure drop was observed to rise significantly. As the hydraulic diameter of the microchannel reactor decreases below approximately 240 μm with a turn number of 350/1.07m, fluid leakage was observed at some joints. Therefore, a compromise must be made when designing the structure of the microchannel reactor between reactor dimensions and pressure drop. There must be a trade-off between dimensions of microreactor system with the benefits of enhanced heat and mass transfer rates, and elevated pressure drops. For a specified volume of catalyst with a constant residence time, a short diameter reaction channel would significantly reduce the pressure drop. This splits the flow into numerous channels, so that the operative cross-sectional area is large and diminishes the pressure drop. Microfabrication techniques can have the ability to grasp reactor designs that combine the intensified mass transfer rates. A multichannel packed bed reactor fabricated by the same technique as the single-channel reactor is an example of such design. The width of each inlet distribution channel is adjusted so that the pressure drop is identical over every channel despite the varying lengths of the distribution channels[95]. Capillary microreactors for biodiesel synthesis seem viable and beneficial for practical use when compared to the conventional reactors; however, the recorded pressure drops were quite high in the capillaries with lengths of 30m. Therefore, the length of the microreactor should be made shorter to avoid problems with high pressure drop[96]. Hu et al.[97] carried out the production of ethanol and C_2 oxygenates in a microchannel reactor over rhodium-manganese catalyst supported by silica. The reaction was conducted at the conditions of 260-300°C and 20-54 bar. The results showed that a CO conversion of 32% and a selectivity towards ethanol of 44.4% could be achieved at a pressure 38 bar. However, it was also observed that when increasing the pressure further to 54 bar, the conversion also increased to 40.5%. In addition, Zhang et al.[98] studied hydrodeoxygenation of bio-oil derived from fast pyrolysis of biomass. Some of the compounds present in the bio-oil sample included ketones, carboxylic acid, aromatics and ethers; these oxygenated groups result in the bio-oil becoming instable with regards to reactivity. The study

evaluated the effect of pressure on hydrodeoxygenation of the sample bio-oil at 650K with a 10 minutes reaction time. Results gathered from this experiment suggested that changes to hydrogen pressure has minute effect on deoxygenation. This may be attributed to the fact that tetralin was used as solvent in the experiments; tetralin is itself an efficient hydrogen donor, and hence it may not be significantly affected by variations in the hydrogen partial pressure.

Conclusions

The need to replace fossil fuels as a form of energy, has led to the utilisation of microreactors for the production of alternative liquid fuels using processes such as biofuel production. The benefits of microreactors in contrast to conventional ones typically used in industrial process include improved mass and heat transfer, shorter reaction times and a more green and sustainable approach. Microreactors have also demonstrated the ability to be scaled up to meet a larger-throughput for industrial applications. Micro-tubular and multi-microchannel reactors have been used for the synthesis of biodiesel which is often a homogeneous catalytic process. These reactors have shown a vast superiority over conventional macroscopic reactors. This is due to the significantly higher product yield and selectivity, as well as shorter reaction times. For heterogeneous catalytic processes, such as FT synthesis, the reactors utilised consist of packed bed, slug flow and coated wall microreactors. Current research has shown that these reactors generate significantly higher conversions, whilst the reactions are catalysed under milder reaction conditions as opposed to the conditions required in conventional bulk reactors. Microplasma reactors present a novel design in this area. They enable the direct partial oxidation of methane to methanol at significantly lower temperatures and pressures when compared to the typical reactors used. This means that micro-plasma reactors can offer the same reactive environment as the conventional reactors at milder conditions.

The current review has highlighted the fact that the implementation of microreactors for the generation of liquid fuels (in view of replacing existing petroleum and diesel fuels), has been valuable in providing technical solutions to the problems associated with conventional fuel processing. Microreactors have begun to operate in remote difficult to access locations for offshore production. This on the other hand has proven difficult to do so with conventional macroscopic reactors. Furthermore, there is great potential for these devices to be applied to generate electrical energy and other renewable fuels. Despite the promising outlook on the implementation of microreactors for liquid fuel production there are still issues that need to be resolved. The scale up of microreactors has not been applied on an industrial scale, and there are often difficulties faced with coating the reactor wall with the catalyst, and these catalysts have to be specially designed to be used in these particular reactors. Moreover,

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replacing the used catalysts can prove to be time consuming and expensive.

The path for future research and development has been paved to explore the variety of different liquid fuel production routes that microreactors can be applied to. Hence, it can be assumed that microreactors can replace conventional ones for liquid fuel production in the near future. Further work can be directed towards implementing microreactors for niche applications like small scale fuel production in remote communities and/or in households for domestic use. In addition, the scaling up of microreactors for industrial use can be explored further. The issues faced with the exploited catalysts for the different reactors can also be researched for further improvements.

Conflicts of interest

The authors declare no conflicts of interest.

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