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Synthesis and imitation of a bio-transformation process path for the gas to liquid systems

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Article Info

Abstract

This article presents the simulation of the bioconversion of syngas produced during natural gas gasification into biodiesel compatible lipids, and compares it to the bio-GTL process to the Fischer-Tropsch synthesis routes in terms of product quality, emission levels, exergy, and energy efficiencies using Aspen Hysys simulation Software. The direct use of natural gas is limited by infrastructure changes necessitated by its use in transportation. The Fischer–Tropsch process, or indirect conversion of natural gas to liquid fuels (GTL), is a complementary strategy (synthesis of syngas or methanol). These liquid fuels and their intermediates have been found to be inefficient and energy-intensive in industrial settings where they are currently manufactured. Bioconversions consume less energy, cost less, and are more product-specific than chemical conversions. The method consisted of two steps: anaerobic syngas conversion to acetic acid via the acetogen Moorella thermoacetica, and aerobic acetic acid conversion to lipids via Yarrowia lipolytica, a genetically engineered oleaginous yeast. With an overall productivity of 34.47 percent and a carbon conversion efficiency of 18.60 percent, the integrated continuous bench-scale reactor system produced 36 percent of C_{16}-C_{18} triacylglycerides directly from synthesis gas. Technically, the newly developed Bio-Gas to Liquid (GTL) pathway is feasible and has the potential to outperform the traditional Fischer–Tropsch process.

Introduction

Government, academia, and industry have all made significant efforts in recent decades to develop environmentally friendly products and processes with increased energy efficiency and low carbon emission [1, 2]. Despite the fact that numerous innovative solutions and technologies have been studied, developed, and adopted (either in their pure form or as blends) to provide alternative fuels, the demand for liquid transportation fuel is expected to rise from 95 million barrels per day in 2015 to 121 million barrels per day in 2040 [3, 4].

Despite the fact that these non-fossil-based fuel alternatives have proven to be reliable in terms of net carbon emissions [5], there are concerns about their economic viability, particularly in terms of infrastructure. Syngas is also fascinating because of the diverse intermediate or supplementary products it produces from a variety of industrial processes, including petroleum refining, steel manufacturing, combustion and partial oxidation processes, steam reforming treatments, and others [6]. Pre-commercial integration of syngas-producing industrialization and fermentation modules for the production of bioethanol has now been investigated several times in China [6, 7].

Natural gas is a more environmentally friendly, more palatable, and multi-functional fuel with abundant reserves around the world. For these peculiar reasons, it is a common crude oil substitute in some application domains.

Nonetheless, for the majority of its compositions, natural gas exists "naturally as a gas," which causes transportation issues [8] of natural gas from its source or refineries to a variety of locations where its various useful products can be used [8-10]. Stringent gas shipping criteria, associated gas flaring, energy supply security, high capital cost, and other environmental hydrocarbon considerations [5, 10-13] all necessitate a search for new ways to use natural gas reserves.

Converting natural gas into liquid transportation fuels [14-17] may provide a potential solution to this impasse. Natural gas, which is primarily composed of methane, can be used as a raw material to produce high-value products through refining or microbial fermentation while lowering the greenhouse effect and alleviating energy shortages [18]. Synthetic gas (CO, CO_2, and H_2) [19], an intermediate product before liquid fuel production, can be made from natural gas. These products can be used to provide renewable alternatives for a variety of purposes [18].

Gas-to-liquids (GTL) has emerged as a commercially viable industry in the last thirty years, providing market diversification to remote natural gas resource owners [20]. Natural gas's high hydrogen-to-carbon ratio also makes it easier to convert carbon feedstock to liquid fuels [21], reducing the amount of CO_2 produced and landmass consumed in comparison to coal and biomass [13]. For many years, scientists have been researching and developing technology to convert natural gas into hydrocarbon liquid fuels. The Fischer–Tropsch (FT) technology has drawn a lot of attention [21] because of the high-value hydrocarbons and related oxygenated compounds (fuels), methanol, and higher alcohols, among other high-value products formed [10]. Despite these advantages, the FT technology has disadvantages such as high energy consumption due to the high temperatures (exothermic) [22] and pressures required, as well as high operational costs, [6, 23], high catalyst supply costs, stationary CO-H_2 ratios, and sample preparation to remove poisonous compounds from the catalysts [6, 10, 24], limiting the energy efficiency of this process, low carbon conversion efficiency (CCE), [24], and low carbon conversion efficiency (CCE), among others Bioconversion has become a viable option as a result of the direct inverse of the disadvantages of FT technology [2, 24]. There are also advantages such as impurity tolerance, insensitivity to the C–H ratio, selective production of desired products, and the bio-conversion process' irreversibility [2].

The scientific and industrial communities are debating a biological methane (or syngas) conversion process that targets valuable compounds such as next-generation fuels or chemical products such as diesel, dimethyl ether, arenes, alcohols, olefins, carboxylic esters, aldehydes, carboxylic acids, ultra-clean gasoline, and high-quality waxes [1, 24, 25]. This technology for developing and converting natural gas to liquid fuels or other chemical products has the potential to transform the natural gas industry by utilising a large portion of the world's natural gas reserves in remote areas [13, 25]. Natural gas methane, landfill methane, biomass, and coal-bed methane have all been converted to a variety of chemicals [8, 11, 13, 17, 24, 26, 27], or in hybrid forms [12, 13, 21].

A unique microbial community known as methanotrophic bacteria performs the Bio-GTL technology [28]. Methanotrophs that have been discovered so far all work aerobically, oxidising methane from natural gas, biogas, or landfill gases. Only the bacterium "M. oxyfera" has been found to be capable of facultatively oxidising methane through a fragmented denitrification pathway. However, this methanotroph is not available in its pure form, limiting its biological and technical research [28]. In a well-established natural process, this growing class of aerobic microorganisms can convert methane to a variety of products such as methanol, formaldehyde, methyl tert-butyl, lipids, which are biomass, ethylene, plastics, and several other industrial precursors [18, 28-32]. This Bio-GTL process, which combines synthetic biology, biocatalysis, and advanced bioengineering, has the potential to be less expensive and more efficient than traditional FT and other chemical processes, with environmental and economic benefits [24].

Several Bio-GTL conversions for various target products and by-products have been carried out. Methanotrophs Methylomicrobium buryatense (5GB1) and the glycogen-knock-out mutant (AP18) were investigated for the production of lipids derived from intracellular membranes for green biodiesel production [32]. By limiting the AP18 strain's glycogen biosynthesis, the researchers were able to increase lipid content by 90%. The cetane number of the lipid produced by M. buryatense was estimated to be 75, which is 50% higher than the biofuel standards demanded by the US and EU.

Hu et al developed an integrated method for converting gaseous substrates to liquids in two stages. Moorella thermoacetica, an anaerobic acetogen, was used to convert syngas to acetic acid in the first stage, and Yarrowia lipolytica, an engineered oleaginous yeast, was used to convert the intermediate acetic acid into liquid chemicals in the second stage. They produced a lipid content of 36%, with an overall productivity of 0.19 gL1h1.

In the production of lipids, [33] used Rhodosporidium toruloides yeast. They achieved lipid content of 0.47 and 0.52 g/g in the absence of oxygen, with productivity of 0.16 and 0.17 g/L.day, respectively. In the presence of oxygen, however, lipidic productivity increased by 0.20 g/L.day, with a lipid content of 0.51 g lipids/g biomass. In comparison to individual n-dodecane and aeration addition (51 percent, w/w and 52 percent, w/w), this combined aeration and n-dodecane addition approach produced a significant 62 percent w/w lipid improvement.

Bao et al. used the Fischer–Tropsch (FT) process, Aspen plus simulation software, and the ICARUS cost evaluator to produce 118,000 bbl/day of diesel, LPG, and naphtha from 1.16 billion SCF/d of natural gas in an integrated simulation and economic analysis of the GTL technology [8]. For natural gas costs of $8 and $5/1000 SCF of natural gas, respectively, the work generated a ROI of 7.4 percent to 19.4 percent.

The purpose of the study is to give a detailed energy efficiency and emission assessment of the bio-GTL process in comparison to the Fischer-Tropsch process. The scope would cover the simulation of the bio-GTL process route synthesis for the two-stage conversion of natural gas to lipids using methanotrophs. Further analyses of the process route will be carried out with respect to the product quality (carbon conversion efficiency and energy efficiencies) in comparison with the FT process route.

Methodology
Feed Composition
The typical composition of the natural gas feedstock is given in Table 1

Table 1: Typical feed composition of NG as used for the study

Composition	Fractions
Methane	95.5%
Ethane	3%
Propane	0.5%
n-Butane	0.4%
Nitrogen	0.6%

Process Simulation

The Process simulation was carried out using Aspen HYSYS, a process modelling tool that is very popular in the oil and gas, gas processing, petroleum refining, and air separation industries. It is used for conceptual design, optimization, business planning, asset management, and performance monitoring.

FT Simulation

For the simulation the NRTL-RK property method was employed. An Autothermal Reforming Reactor (ATR), which combines steam reforming and methane oxidation, is claimed to be the best route for syngas production [34] and has been chosen for this study. An adiabatic pre-reformer was used to avoid the possibility that the ATR will operate as a steam cracker, producing olefins from higher hydrocarbons in the feed. The temperature therefore ranged between 350 and 550°C, in which all higher hydrocarbons are converted [35].

In this study, natural gas and water was preheated to 455°C before being fed into the adiabatic pre-reformer. Despite the exothermic equilibrium reactions, the overall reactions were endothermic, with an estimated outlet temperature of 416°C. Before entering the adiabatic Autothermal reformer, the pre-reformer outlet stream was mixed with recycled flue gas from the FT unit and heated to 675°C in a fired heater (ATR). The oxygen was preheated to 200°C and was fed to the ATR as well. The ATR is the primary reactor in the production of synthesis gas, and it is where the three major reactions take place.

The net reactions were exothermic due to the large heat generated by combustion a reaction, and the ATR's outlet temperature will be around 1000ºC. To remove the majority of the CO_2 from the syngas, a high-pressure MDEA (Methyl Diethanolamine) is used as an absorbent. The main product of ATR was a mixture of hydrogen and carbon monoxide, and an H_2/CO ratio of around 2-2.3 is desired for maximum conversion to liquid fuels in the subsequent FT reactor (Figure 2). A small amount of CO_2 was recycled to the ATR to set this ratio. This prevented too much CO from being converted to CO_2 as a result of the reaction.

Bio-GTL Simulation
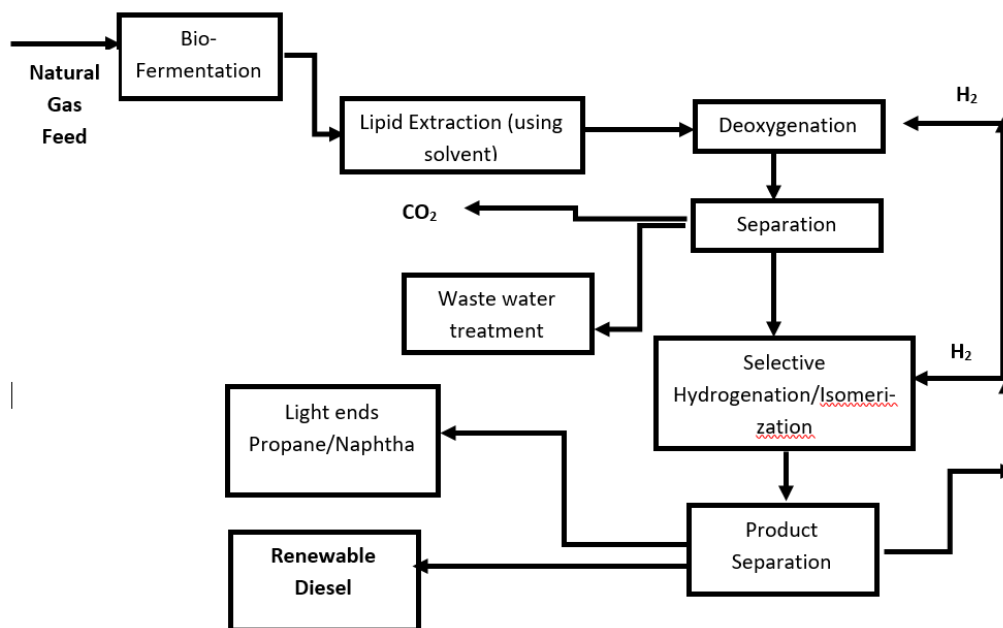
Fig 1: Bio-GTL Process routes

The NRTL-RK property method was chosen for this purpose. The natural gas bio-fermentation stage, which is in a real sense, is always a fed-batch or semi-continuous process with typical residence time taking between 48 – 96 hours will be simulated as a continuous process using the CSTR block.

A few novel concepts were used in this study, allowing the simulation of the bio-GTL process to be successfully implemented. *M. thermoacetica* was first used as a model organism to produce acetic acid. This was done due to its extremely high autotrophic discharge of acetyl coenzyme A, which ultimately produces acetate at significantly high rates and almost hypothetical yields through the classical Wood–Ljungdahl path [23]. The simulation was operated at optimal

temperatures of 60 ℃. This makes the thermophilic organism industrially attractive because they require lesser energy to cool before feeding the bioreactor compared with the other model acetogens, *Clostridium ljungdahlii* (T_{opt} = 37 ℃) and *Acetobacterium woodii* (T_{opt} = 30 ℃) [31].

Results and Discussion

100kg/hr was used for the simulation of Bio-GTL based on the direct conversion of CO and H_2 to acetic acid via batch fermentation and this is finally converted to lipids fraction with an observed 36% yield of lipids in a broth concentration of 25 g/L. Figure 2 shows the product distribution of the lipids obtained which are mainly triglycerides consisting of

palmitic acid, palmitoleic acid, stearic acid, oleic acid, and linoleic acids respectively. These fatty acids were further hydro-processed with the addition of H_2 gas corresponding to 50 kg/hr at 2 MPa and 350 ℃ without any catalyst used.

The product distribution of the various liquid fuels components produced by the two different synthesis routes was compared. This distribution is depicted in Figure 2 below for both synthesis routes, as indicated by their curve lines. For the bio-GTL pathway, no LPG fraction was obtained. The absence of C_5–C_{14} components, as well as the presence of heavier liquid fraction components, support the specificity typically associated with bio-processes such as enzyme-catalysed reactions and fermentation processes.

LPG fraction is more likely to be formed in the FT process because of the higher formation of the lighter components. As the carbon chain length increased, the mass fraction of liquid fuels decreased. This could be attributed to the cobalt-based catalyst's influence on the different rates of formation [36], [37]. Since more heavy liquid fractions are formed using the bio-GTL process, which can be further cracked to produce lighter liquid fuel fractions (typically gasoline and diesel) with high yields of conversion, the bio-GTL route is preferred for production.
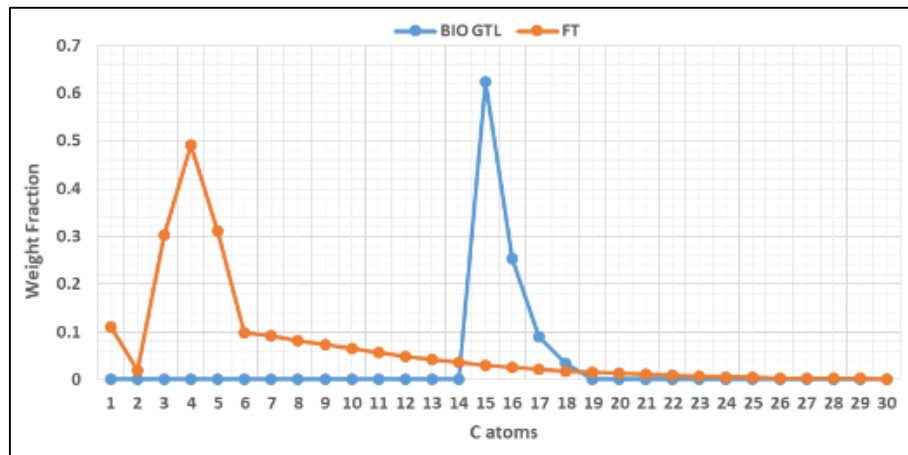
Fig 2: Comparison between bio-GTL vs FT product distribution
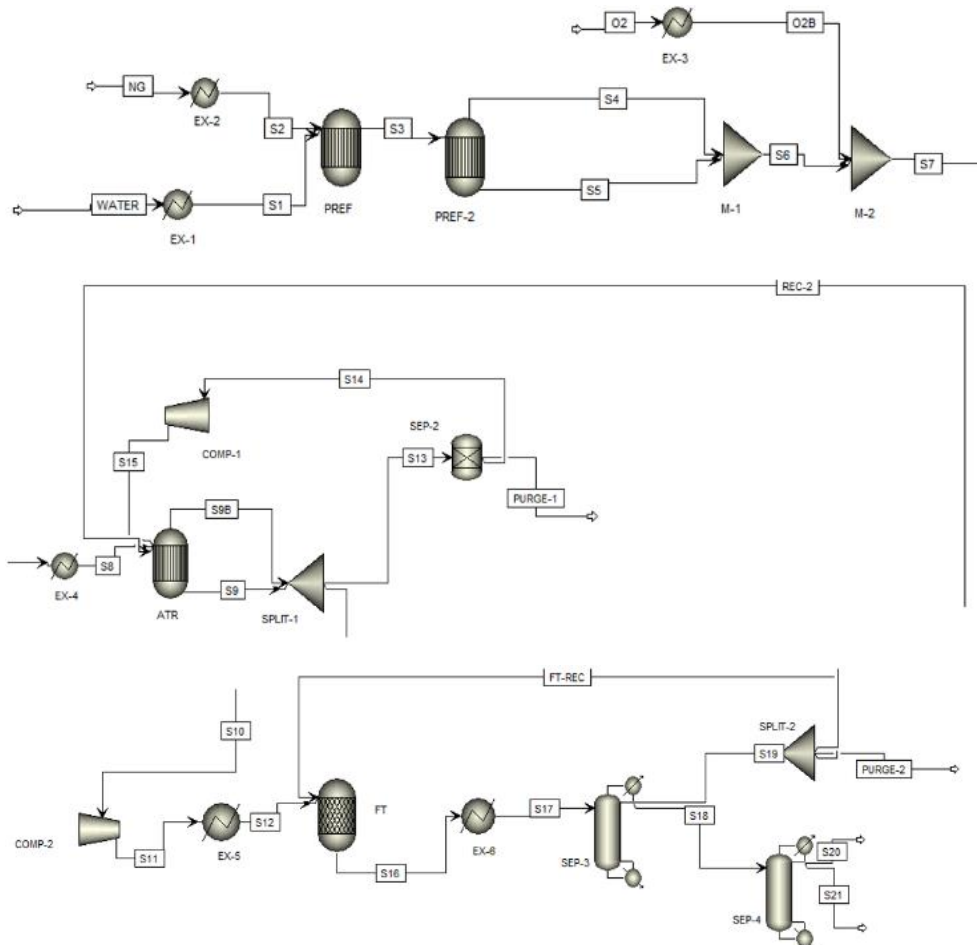
Fig 3: Flowsheet for the FT-GTL Synthesis Simulation
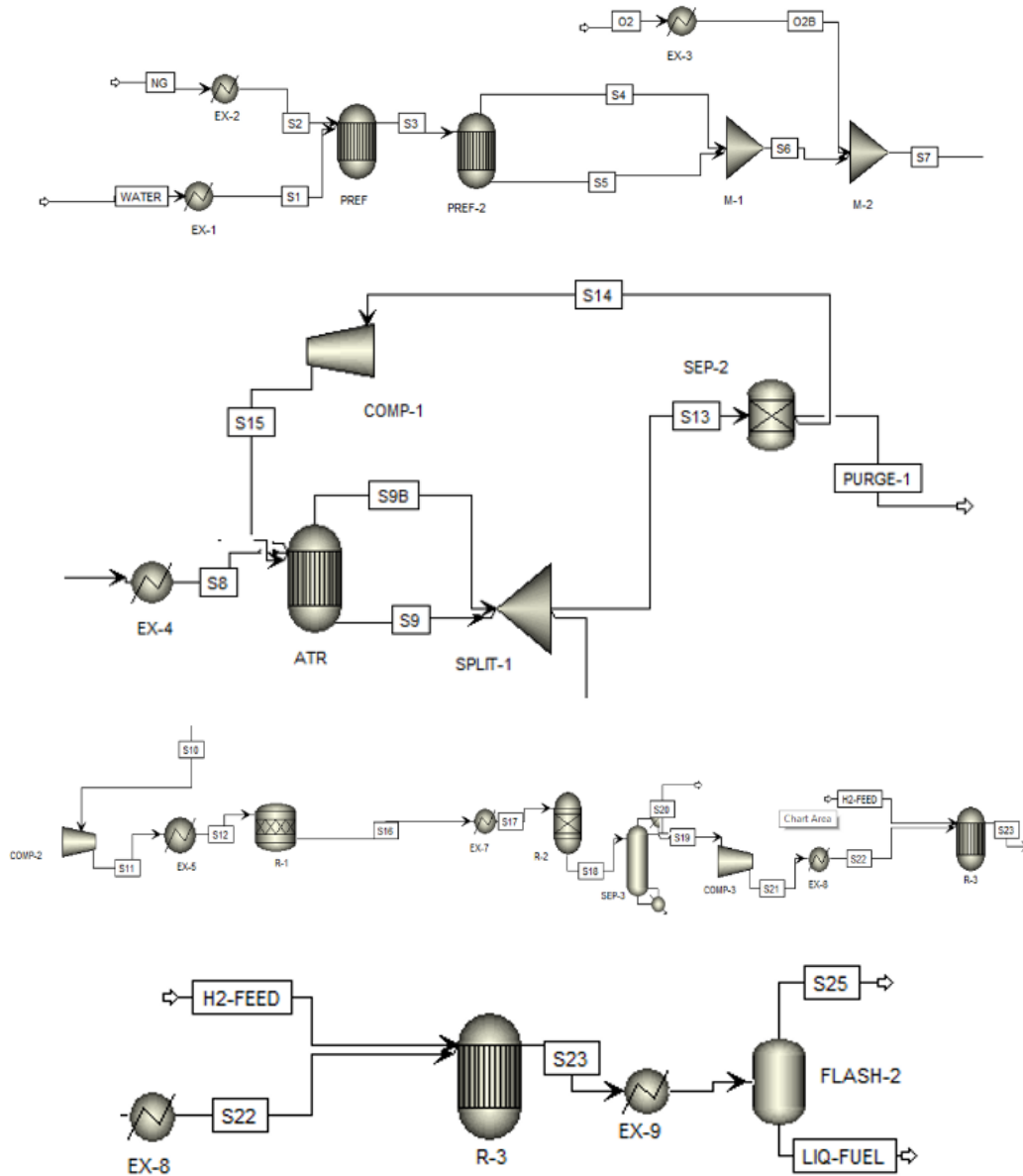
Fig 4: Flowsheet for the Bio-GTL Synthesis Simulation
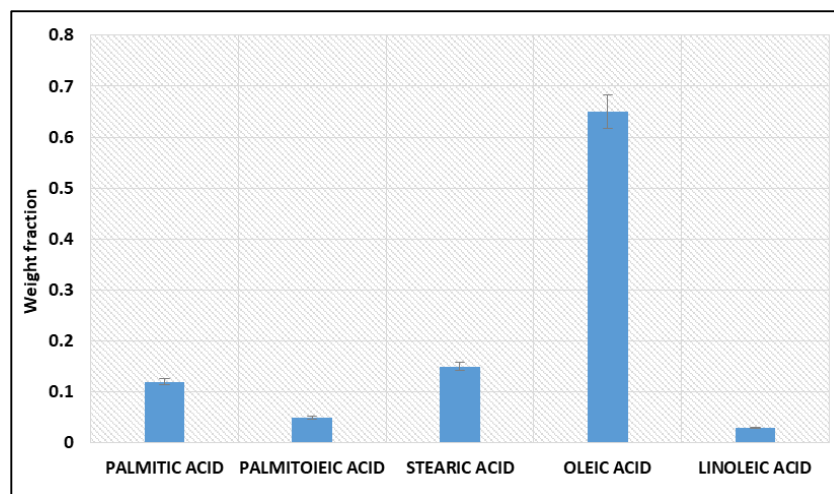
Fig 5: Product distribution of fatty acids in the lipids biomass

From the Figure, oleic has the highest weight fraction of about 65% which is due to the higher selectivity of the organism used towards producing unsaturated hydrocarbons from the biomass. Other products in descending order include stearic acid (15%), palmitic acid (12%), palmitoleic acid (5%), and linoleic acid (3%).

Material and Energy Balance Results for the Bio-GTL Synthesis

Table 3 (Appendix) shows the results of the material and energy balances obtained from the Aspen Plus simulation.
From the material and energy balance result presented in Table 2, the bio-GTL process route produced an overall conversion of 34.47% with most of the products distributed within the C_{15} to C_{18} range thereby providing more feedstock for further cracking into lighter liquid fuels. Furthermore, the bio-GTL process is seen to be a relatively low-energy process.

Conversion Efficiency of the Bio-GTL Synthesis

The calculation of carbon conversion efficiency which is another indication of the technical feasibility of the different routes was calculated using Equation 1:

$$\text{Carbon Efficiency (\%)} = \frac{\text{No. of moles of product} \times \text{No. of carbon atoms in product}}{\text{No. of moles of feed} \times \text{No. of C atoms in feed}}$$

Table 2: Carbon conversion efficiency calculation for BIO-GTL process

Calculation of the carbon conversion efficiency			
Feed			
Species containing C atoms present in the feed	Number of C atoms	Molar amounts (kmol/hr)	
CH_4	1	5.669681	
C_2H_6	2	0.1781052	
C_3H_8	3	0.0296841	
C_4H_{10}	4	0.0237473	
10		**5.9012176**	
			59.012176
Products			
Species containing C atoms present in the product	Number of C atoms	Molar amounts (kmol/hr)	
C_{15}	15	0.0850831	
C_{16}	16	0.0325949	
C_{17}	17	0.0107783	
C_{17-2}	17	0.0000001	
C_{18}	18	0.0037713	
83		**0.1322278**	
			10.97490516
		Efficiency	**18.60%**

The low carbon conversion efficiency is attributable to the fact that the bio-GTL technology is still in its infancy. When subsequent results of laboratory research made at engineering micro-organisms with wider specificity have been implemented, it is believed that the carbon conversion efficiency will increase significantly to the extent of competing favourably with the values obtained for the FT synthesis route.

Table 4 compares other process inhibitors (microorganisms) used for lipid content and carbon conversion, as well as their substrates, products, and percentage conversions. *Yarrowia lipolytica* provided superior conversions of acetic acid to lipids with a lipid content of at least 36 percent, based on comparisons [31, 38]. This is analogous to the outcome of this work for a continuous process. However, the results from batch processes [39-41] demonstrating higher conversions than the results obtained in this study (18.60%) provide additional grounds for research using microorganisms such as *Methylosinus trichosporium* OB3b, *Methylosinus trichosporium* OB3b (using 0.5mM EDTA as an inhibitor), and Methanotrophic Consortium (40 mM of NH4Cl as an inhibitor). Using *Rhodosporidium toruloides*, Guerreiro *et al.*, [33] demonstrated that a higher lipid accumulation (62 %) was possible despite the differing substrates and unreported material flow process. *Methylomicrobium buryatense* 5GB1,

as utilised by Fei *et al.*, [32] demonstrated a 90 % increase in lipid content. Even though the actual amount of product was not reported, this microorganism can be considered for the bio-GTL process employed in this study.

Conclusion

The Bio-GTL process route was successfully synthesized and simulated. A 12.84 % feed conversion to liquid fuel was achieved through FT synthesis, as was a wide range of products, with a higher concentration in the LPG fraction. At 45.02 % conversion efficiency, this technology reached maturity. On the other hand, a conversion of 34.47 % was achieved via the bio-GTL route, whereas most products were distributed in the C_{15}–C_{18} range thereby increasing the supply of raw materials for the production of lighter liquid fuels. This technology is still in its infancy, as evidenced by its low carbon efficiency of only 18.6%, however, it can be concluded from the results of this work that the novel Bio-GTL synthesis route developed is technically viable with great potential of competing favourably with the conventional Fischer – Tropsch process route. If further research on improving the process such as; engineering micro-organisms with wider specificity and so on are carried out.

Appendix

Table 3: Heat and material stream balance for Bio-GTL synthesis

Stream ID		H2-Feed	LIQ-Fuel	NG	O2	O2B	Purge-1	S1	S2	S3	S4	S6	S7	S8	S9B	S10
From			FLASH-2				EX-3	SEP-2	EX-1	EX-2	PREF	PREF-2	M-1	M-2	EX-4	ATR	SPLIT-1
To		R-3		EX-2	EX-3	M-2		PREF	PREF	PREF-2	M-1	M-2	EX-4	ATR	SPLIT-1	COMP-2
Phase		Vapor	Liquid	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	VAPOR	VAPOR
*** All Phases ***																
Mass Flow	kg/hr															
CO		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.1060742	.1060274	.1060274	.1060274	.1060274	145.5274	119.6235
CO2		0.0	0.0	0.0	0.0	0.0	15.01497	0.0	0.0	6.622293	6.621761	6.621761	6.621761	6.621761	85.49539	70.27721
O2		0.0	0.0	0.0	310.0000	310.0000	0.0	0.0	0.0	2.7910E-29	2.7910E-29	2.7910E-29	310.0000	310.0000	46.53092	38.24842
H2O		0.0	0.0	0.0	0.0	0.0	0.0	30.80000	0.0	25.31014	25.31061	25.31061	25.31061	25.31061	231.1766	190.0272
N2		0.0	0.0	.9978690	0.0	0.0	0.0	0.0	.9978690	.9978690	.9978690	.9978690	.9978690	.9978690	1.213953	.9978690
CH4		0.0	0.0	90.95733	0.0	0.0	0.0	0.0	90.95733	97.12905	97.12927	97.12927	97.12927	97.12927	1.42100E-7	1.16806E-7
H2		25.00000	2.00762E-5	0.0	0.0	0.0	0.0	0.0	0.0	.6152106	.6151030	.6151030	.6151030	.6151030	8.021253	6.593470
Ethene		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.24103E-6	3.24103E-6	3.24103E-6	3.24103E-6	3.24103E-6	3.94286E-6	3.24103E-6
1-Butene		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.1316E-11	4.1316E-11	4.1316E-11	4.1316E-11	4.1316E-11	4.1316E-11	3.3962E-11
Propene		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.79007E-8	4.79007E-8	4.79007E-8	4.79007E-8	4.79007E-8	5.82733E-8	4.79007E-8
1-PEN-01		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.9118E-14	2.9118E-14	2.9118E-14	2.9118E-14	2.9118E-14	2.9118E-14	2.3935E-14
C2		0.0	0.0	5.355558	0.0	0.0	0.0	0.0	5.355558	.0193385	.0193385	.0193385	.0193385	.0193385	.0235262	.0193385
C3		0.0	0.0	1.308970	0.0	0.0	0.0	0.0	1.308970	1.94470E-5	1.94470E-5	1.94470E-5	1.94470E-5	1.94470E-5	2.36581E-5	1.94470E-5
C4		0.0	0.0	1.380277	0.0	0.0	0.0	0.0	1.380277	1.69363E-8	1.69363E-8	1.69363E-8	1.69363E-8	1.69363E-8	2.06037E-8	1.69363E-8
C15		0.0	17.77748	0.0	0.0	0.0	0.0	0.0	0.0	8.5412E-44	8.5412E-44	8.5412E-44	8.5412E-44	8.5412E-44	8.5412E-44	7.0208E-44
C16		0.0	7.332480	0.0	0.0	0.0	0.0	0.0	0.0	5.3147E-47	5.3147E-47	5.3147E-47	5.3147E-47	5.3147E-47	5.3147E-47	4.3687E-47
C17		0.0	2.584976	0.0	0.0	0.0	0.0	0.0	0.0	2.8961E-50	2.8961E-50	2.8961E-50	2.8961E-50	2.8961E-50	2.8961E-50	2.3806E-50
C18		0.0	.9587072	0.0	0.0	0.0	0.0	0.0	0.0	1.6322E-53	1.6322E-53	1.6322E-53	1.6322E-53	1.6322E-53	1.6322E-53	1.3417E-53
Palmitic		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.4044E-52	6.4044E-52	6.4044E-52	6.4044E-52	6.4044E-52	6.4044E-52	5.2644E-52
Stearic		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.7283E-58	3.7283E-58	3.7283E-58	3.7283E-58	3.7283E-58	3.7283E-58	3.0647E-58
Oleic		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1585E-55	1.1585E-55	1.1585E-55	1.1585E-55	1.1585E-55	1.1585E-55	9.5231E-56
Linoleic		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.3168E-60	2.3168E-60	2.3168E-60	2.3168E-60	2.3168E-60	2.3168E-60	1.9044E-60
C17-2		0.0	3.16275E-5	0.0	0.0	0.0	0.0	0.0	0.0	7.9373E-53	7.9373E-53	7.9373E-53	7.9373E-53	7.9373E-53	7.9373E-53	6.5244E-53
Acetate		0.0	.7852588	0.0	0.0	0.0	0.0	0.0	0.0	5.88523E-7	5.88523E-7	5.88523E-7	5.88523E-7	5.88523E-7	7.15964E-7	5.88523E-7
Total Flow	cum/hr	16.66007	.0392014	2.103040	19.05567	19.05567	2.251329	4.140166	4.890080	9.405543	9.405263	9.405262	44.68505	18.92282	167.9239	138.0334
Massvfra		1.000000	0.0	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000	1.000000
Masssfra		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Density	kg/cum	1.500594	750.9663	47.55021	16.26813	16.26813	6.669379	7.439314	20.44956	13.90669	13.90711	13.90711	9.864598	23.29463	3.084666	3.084666
Temperature	C	50.00000	63.98371	40.00000	200.0000	200.0000	3695.170	455.0000	455.0000	437.8759	437.8572	437.8571	336.1008	675.0000	3695.175	3695.175
Pressure	bar	20.00000	1.013000	73.50000	20.00000	20.00000	50.00000	5.00000	73.50000	50.00000	50.00000	50.00000	20.00000	73.50000	50.00000	50.00000

Table 3 CONT: Heat and material stream balances for Bio-GTL synthesis

Stream ID		S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	Water
From		COMP-2	EX-5	SPLIT-1	SEP-2	COMP-1	R-1	EX-7	R-2	SEP-3	SEP-3	COMP-3	EX-8	R-3	EX-9	FLASH-2	
To		EX-5	R-1	SEP-2	COMP-1	ATR	EX-7	R-2	SEP-3	COMP-3		EX-8	R-3	EX-9	FLASH-2		EX-1
Phase		Vapor	Mixed	Vapor	Vapor	Vapor	Mixed	Mixed	Mixed	Mixed	Mixed	Liquid	Mixed	Vapor	Mixed	Vapor	Liquid
*** All Phases ***																	
Mass Flow	kg/hr																
CO		119.6235	119.6235	25.90523	25.90523	25.90523	9.569882	9.569882	9.569882	.0478494	9.522033	.0478494	.0478494	0.0	0.0	0.0	0.0
CO2		70.27721	70.27721	15.21890	.2039333	.2039333	90.52005	90.52005	90.52005	.4526003	90.06745	.4526003	.4526003	0.0	0.0	0.0	0.0
O2		38.24842	38.24842	8.282524	8.282524	8.282524	38.24842	38.24842	38.24842	0.0	38.24842	0.0	0.0	0.0	0.0	0.0	0.0
H2O		190.0272	190.0272	41.14933	41.14933	41.14933	181.7408	181.7408	181.7408	.9087041	180.8321	.9087041	.9087041	0.0	0.0	0.0	30.8000
N2		.9978690	.9978690	.2160836	.2160836	.2160836	.9978690	.9978690	.9978690	0.0	.9978690	0.0	0.0	0.0	0.0	0.0	0.0
CH4		1.1681E-7	1.1681E-7	2.5295E-8	2.5295E-8	2.5295E-8	1.16806E-7	1.1681E-7	1.16806E-7	0.0	1.1681E-7	0.0	0.0	0.0	0.0	0.0	0.0
H2		6.593470	6.593470	1.427788	1.427788	1.427788	.5274776	.5274776	.5274776	0.0	.5274776	0.0	0.0	24.62079	24.62079	24.62077	0.0
ETHENE		3.2410E-6	3.2410E-6	7.0183E-7	7.0183E-7	7.0183E-7	3.24103E-6	3.2410E-6	3.2410E-6	0.0	3.2410E-6	0.0	0.0	0.0	0.0	0.0	0.0
1-BUTENE		3.3962E-11	3.3962E-11	7.3543E-12	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PROPENE		4.79007E-8	4.79007E-8	1.03727E-8	1.03727E-8	1.0373E-8	4.79007E-8	4.79007E-8	4.79007E-8	0.0	4.79007E-8	0.0	0.0	0.0	0.0	0.0	0.0
1-PEN-01		2.3935E-14	0.0	5.1830E-15	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C2		.0193385	.0193385	4.18767E-3	4.18767E-3	4.1877E-3	.0193385	.0193385	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C3		1.94470E-5	1.94470E-5	4.21115E-6	4.21115E-6	4.2115E-6	1.9447E-5	1.9447E-5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C4		1.69363E-8	1.69363E-8	3.66746E-9	3.66746E-9	3.6675E-9	1.69363E-8	1.69363E-8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C15		7.0208E-44	0.0	1.5203E-44	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	18.07329	18.07329	.2958057	0.0
C16		4.3687E-47	0.0	9.4602E-48	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.380996	7.380996	.0485154	0.0
C17		2.3806E-50	0.0	5.1551E-51	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.591900	2.591900	6.9243E-3	0.0
C18		1.3417E-53	0.0	2.9053E-54	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.9598047	.9598047	1.0975E-3	0.0
PALMITIC		5.2644E-52	0.0	1.1400E-52	0.0	0.0	0.0	0.0	6.375969	6.375969	0.0	6.375969	6.375969	0.0	0.0	0.0	0.0
STEARIC		3.0647E-58	0.0	6.6364E-59	0.0	0.0	0.0	0.0	5.625855	5.625855	0.0	5.625855	5.625855	0.0	0.0	0.0	0.0
OLEIC		9.5231E-56	0.0	2.0622E-56	0.0	0.0	0.0	0.0	24.37871	24.37871	0.0	24.37871	24.37871	0.0	0.0	0.0	0.0
LINOLEIC		1.9044E-60	0.0	4.1239E-61	0.0	0.0	0.0	0.0	1.125171	1.125171	0.0	1.125171	1.125171	0.0	0.0	0.0	0.0
C17-2		6.5244E-53	0.0	1.4128E-53	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1719E-5	3.1719E-5	9.1931E-8	0.0
ACETATE		5.88523E-7	5.88523E-7	1.27442E-7	1.27442E-7	1.2742E-7	104.1631	104.1631	66.67680	0.0	66.67680	0.0	0.0	10.28804	10.28804	9.502782	0.0
Total Flow	cum/hr	140.4991	352.7215	29.89086	27.63950	22.62679	129.4330	104.2348	104.3547	.3087959	104.0961	.0458307	.1922296	32.42567	17.54325	342.3776	.0309872
MASSVFRA		1.000000	.6599727	1.000000	1.000000	1.000000	.3696988	.3342720	.3338037	.0108777	.3663817	0.0	.0433629	1.000000	.4352909	1.000000	0.0
MASSSFRA		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Density	kg/cum	3.030531	1.207148	3.084690	2.792709	3.411402	3.289633	4.084885	4.080188	126.0213	3.716489	849.0989	202.4395	1.971119	3.643272	.1006956	993.9570
Temperature	C	3684.227	60.00000	3695.175	3695.170	3950.062	60.00000	38.00000	38.00000	38.00000	38.00000	38.71773	350.0000	350.0000	70.00000	63.98371	25.00000
Pressure	bar	48.98700	1.013000	50.00000	50.00000	65.00000	1.013000	1.013000	1.013000	1.013000	1.013000	20.00000	20.00000	20.00000	20.00000	1.013000	25.00000

Table 3: A comparison of carbon conversion efficiencies for several bio-GTL conversions

Substrate(s)	Process (Inhibitors)	Feeding mode	Product	Product Titre	Result	References
Natural gas, Acetic acid	Moorella thermoacetica, Yarrowia lipolytica	Continuous	Acetic Acid, Lipids	NR	36% lipid content	**This work**
Natural gas	Micro-organism – Methylomicrobium buryatense 5GB1	Continuous	Lipids	0.0454 g/L.h	90% enhancement of lipid content	Fei et al., [32]
Methane	Methylosinus trichosporium OB3b	NR	Methanol	1.1g/L	64% carbon conversion	Duan et al., [39]
Methane	Methylosinus trichosporium OB3b (0.5mM EDTA)	Batch	Methanol	49.0 mg/L·h	75.2% carbon conversion	Hwang et al., [40]
Landfill cover soil	Methanotrophic Consortium (40 mM of NH4Cl)	Batch	Methanol	9.0 μmol/h mg cell	80% carbon conversion	Han et al., [41]
Acetic Acid	Yarrowia lipolytica	Continuous	Lipids	0.19 g/L.h	36 % lipid content	Hu et al., [31]
Acetic Acid	Yarrowia lipolytica	Batch	Lipids	12.4 g/L	40% lipid content	Fontannile et al., [38]
Biomass	Rhodosporidium toruloides	NR	Lipids	0.20 g/L.day	62 % lipid accumulation	Guerreiro et al., [33]

*NR-Not Reported

References

1. Y An, et al. Advances in direct production of value-added chemicals via syngas conversion', Sci. China Chem. 2017; 60(7):887-903, Jul. Doi: 10.1007/s11426-016-0464-1.
2. A Grimalt-Alemany, IV Skiadas, HN Gavala. Syngas biomethanation: state-of-the-art review and perspectives, Biofuels, Bioprod. Bioref. 2018; 12(1):139-158. doi: 10.1002/bbb.1826.
3. International Energy Outlook 2021 - US. Energy Information Administration (EIA)'. https://www.eia.gov/outlooks/ieo/ (accessed Mar. 11, 2022).
4. X Sun, HK Atiyeh, RL Huhnke, RS Tanner. Syngas fermentation process development for production of biofuels and chemicals: A review, Bioresource Technology Reports. 2019; 7:100279. DOI: 10.1016/j.biteb.2019.100279.
5. O Onel, AM Niziolek, JA Elia, RC Baliban, CA Floudas. Biomass and Natural Gas to Liquid Transportation Fuels and Olefins (BGTL+C2_C4): Process Synthesis and Global Optimization', Ind. Eng. Chem. Res. 2015; 54(1):359-385. DOI: 10.1021/ie503979b.
6. K Asimakopoulos, HN Gavala, IV Skiadas. Reactor systems for syngas fermentation processes: A review, Chemical Engineering Journal. 2018; 348:732-744. DOI: 10.1016/j.cej.2018.05.003.
7. DW Griffin, MA Schultz. Fuel and chemical products from biomass syngas: A comparison of gas fermentation to thermochemical conversion routes', Environ. Prog. Sustainable Energy. 2012; 31(2):219-224, Jul. DOI: 10.1002/ep.11613.
8. ND Parkyns, CI Warburton, JD Wilson. Natural gas conversion to liquid fuels and chemicals: Where does it stand, Catalysis Today. 1993; 18(4):385-442. DOI: 10.1016/0920-5861(93)80062-6.
9. B Bao, MM El-Halwagi, NO Elbashir, 'Simulation, integration, and economic analysis of gas-to-liquid processes', Fuel Processing Technology. 2010; 91(7):703-713, Jul. Doi: 10.1016/j.fuproc.2010.02.001.
10. M Ao, GH Pham, J Sunarso, MO Tade, S Liu. Active Centers of Catalysts for Higher Alcohol Synthesis from Syngas: A Review', ACS Catal. 2018; 8(8):7025-7050. Doi: 10.1021/acscatal.8b01391.
11. X Zhao, et al. Conversion of landfill gas to liquid fuels through a TriFTS (tri-reforming and Fischer–Tropsch synthesis) process: a feasibility study', Sustainable Energy Fuels. 2019; 3(2):539-549. Doi: 10.1039/C8SE00344K.
12. RC Baliban, JA Elia, CA Floudas. Biomass and Natural Gas to Liquid Transportation Fuels: Process Synthesis, Global Optimization, and Topology Analysis, Ind. Eng. Chem. Res. 2013; 52(9):3381-3406. Doi: 10.1021/ie3024643.
13. JA Elia, RC Baliban, CA Floudas. Nationwide, Regional, and Statewide Energy Supply Chain Optimization for Natural Gas to Liquid Transportation Fuel (GTL) Systems', Ind. Eng. Chem. Res. 2014; 53(13):5366-5397. Doi: 10.1021/ie401378r.
14. RG dos Santos, AC Alencar. Biomass-derived syngas production via gasification process and its catalytic conversion into fuels by Fischer Tropsch synthesis: A review', International Journal of Hydrogen Energy. 2020; 45(36):18114-18132. doi: 10.1016/j.ijhydene.2019.07.133.
15. I Onwukwe Stanley. Gas-to-Liquid technology: Prospect for natural gas utilization in Nigeria', Journal of Natural Gas Science and Engineering. 2009; 1(6):190-194. Doi: 10.1016/j.jngse.2009.12.001.
16. YH Kim, KW Jun, H Joo, C Han, IK Song. A simulation study on gas-to-liquid (natural gas to Fischer–Tropsch synthetic fuel) process optimization, Chemical Engineering Journal. 2009; 155(1-2):427-432. Doi: 10.1016/j.cej.2009.08.018.
17. T Reddy Keshav, S Basu. Gas-to-liquid technologies: India's perspective', Fuel Processing Technology. 2007; 88(5):493-500. Doi: 10.1016/j.fuproc.2006.12.006.
18. S Wang, Z An, ZW Wang. Bioconversion of methane to chemicals and fuels by methane-oxidizing bacteria', in Advances in Bioenergy. 2020; 5:169-247. Doi: 10.1016/bs.aibe.2020.04.005.
19. J Phillips, R Huhnke, H Atiyeh. Syngas Fermentation: A Microbial Conversion Process of Gaseous Substrates to Various Products', Fermentation. 2017; 3(2):28. Doi: 10.3390/fermentation3020028.
20. DA Wood, C Nwaoha, BF Towler. Gas-to-liquids (GTL): A review of an industry offering several routes for monetizing natural gas', Journal of Natural Gas Science and Engineering. 2012; 9:196-208. Doi: 10.1016/j.jngse.2012.07.001.
21. RC Baliban, JA Elia, R Misener, CA Floudas. Global optimization of a MINLP process synthesis model for

thermochemical based conversion of hybrid coal, biomass, and natural gas to liquid fuels', Computers & Chemical Engineering. 2012; 42:64-86. Doi: 10.1016/j.compchemeng.2012.03.008.

22. K Chen, *et al*. Functionalized Carbon Materials in Syngas Conversion, Small. 2021; 17(48):2007527, Dec. Doi: 10.1002/smll.202007527.

23. IS Al Rowaihi, *et al*. A two-stage biological gas to liquid transfer process to convert carbon dioxide into bioplastic', Bioresource Technology Reports. 2018; 1:61-68. Doi: 10.1016/j.biteb.2018.02.007.

24. Q Fei, MT Guarnieri, L Tao, LML Laurens, N Dowe, PT Pienkos. Bioconversion of natural gas to liquid fuel: Opportunities and challenges', Biotechnology Advances. 2014; 32(3):596-614. doi: 10.1016/j.biotechadv.2014.03.011.

25. RJ Conrado, R Gonzalez. Envisioning the Bioconversion of Methane to Liquid Fuels, Science. 2014; 343(6171):621-623. Doi: 10.1126/science.1246929.

26. X Yang, X Su, D Chen, T Zhang, Y Huang. Direct conversion of syngas to aromatics: A review of recent studies', Chinese Journal of Catalysis. 2020; 41(4):561-573. doi: 10.1016/S1872-2067(19)63346-2.

27. M Gharibi, FT Zangeneh, F Yaripour, S Sahebdelfar, Nanocatalysts for conversion of natural gas to liquid fuels and petrochemical feedstocks', Applied Catalysis A: General. 2012; 443-444:8-26. Doi: 10.1016/j.apcata.2012.06.039.

28. P Dürre, BJ Eikmanns. C1-carbon sources for chemical and fuel production by microbial gas fermentation', Current Opinion in Biotechnology. 2015; 35:63-72. Doi: 10.1016/j.copbio.2015.03.008.

29. IY Hwang, *et al*. Biocatalytic Conversion of Methane to Methanol as a Key Step for Development of Methane-Based Biorefineries', Journal of Microbiology and Biotechnology. 2014; 24(12):1597-1605. Doi: 10.4014/jmb.1407.07070.

30. K Khosravi-Darani, ZB Mokhtari, T Amai, K Tanaka. Microbial production of poly(hydroxybutyrate) from C1 carbon sources', Appl Microbiol Biotechnol. 2013; 97(4):1407-1424. Doi: 10.1007/s00253-012-4649-0.

31. P Hu, *et al*. Integrated bioprocess for conversion of gaseous substrates to liquids', Proc. Natl. Acad. Sci. USA. 2016; 113(14):3773-3778. Doi: 10.1073/pnas.1516867113.

32. Q Fei, AW Puri, H Smith, N Dowe, Philip T Pienkos. Enhanced biological fixation of methane for microbial lipid production by recombinant Methylomicrobium buryatense', Biotechnol Biofuels. 2018; 11(1):129. Doi: 10.1186/s13068-018-1128-6.

33. F Guerreiro, A Constantino, E Lima-Costa, S Raposo. A new combined approach to improved lipid production using a strictly aerobic and oleaginous yeast', Eng. Life Sci. 2019; 19(1):47-56. doi: 10.1002/elsc.201800115.

34. P Bakkerud. Update on synthesis gas production for GTL', Catalysis Today - Catal Today. 2005; 106:30-33. Doi: 10.1016/j.cattod.2005.07.147.

35. RC Brown, 'Process Intensification through Directly Coupled Autothermal Operation of Chemical Reactors', Joule. 2020; 4(11):2268-2289. doi: 10.1016/j.joule.2020.09.006.

36. AR De la Osa, A Romero, F Dorado, JL Valverde, P Sánchez. Influence of Cobalt Precursor on Efficient Production of Commercial Fuels over FTS Co/SiC Catalyst', Catalysts. 2016; 6(7):7. Doi: 10.3390/catal6070098.

37. T Lin, *et al*. Cobalt Carbide Nanocatalysts for Efficient Syngas Conversion to Value-Added Chemicals with High Selectivity', Acc. Chem. Res. 2021; 54(8):1961-1971. doi: 10.1021/acs.accounts.0c00883.

38. C Duan, M Luo, X Xing. High-rate conversion of methane to methanol by Methylosinus trichosporium OB3b', Bioresource Technology. 2011; 102(15):7349-7353. Doi: 10.1016/j.biortech.2011.04.096.

39. IY Hwang, *et al*. Batch Conversion of Methane to Methanol Using Methylosinus trichosporium OB3b as Biocatalyst', Journal of Microbiology and Biotechnology. 2015; 25(3):375-380. Doi: 10.4014/jmb.1412.12007.

40. JS Han, CM Ahn, B Mahanty, CG Kim. Partial Oxidative Conversion of Methane to Methanol Through Selective Inhibition of Methanol Dehydrogenase in Methanotrophic Consortium from Landfill Cover Soil', Appl Biochem Biotechnol. 2013; 171(6):1487-1499. Doi: 10.1007/s12010-013-0410-0.

41. P Fontanille, V Kumar, G Christophe, R Nouaille, C Larroche. Bioconversion of volatile fatty acids into lipids by the oleaginous yeast Yarrowia lipolytica', Bioresource Technology. 2012; 114:443-449. doi: 10.1016/j.biortech.2012.02.091.