

# Performance Analysis of Integral Process of Bio-Oil Production, Bio-Oil Upgrading, and Hydrogen Production from Sewage Sludge

Lida Simasatitkul<sup>1,\*</sup>, Apiwat Lakkhanasombut<sup>1</sup>, Worawit Morin<sup>1</sup>, Supachai Jedsadajerm<sup>1</sup>, Suksun Amornraksa<sup>2</sup>, Karittha Im-orb<sup>3</sup>

<sup>1</sup>Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Thailand.

<sup>2</sup>The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok, Thailand.

<sup>3</sup>Program in Food Process Engineering, Faculty of Food-Industry, King Mongkut's Institute of Technology Ladkrabang, Thailand.

**Abstract.** This research investigated the production of bio-oil through the hydrothermal liquefaction (HTL) process using sewage sludge from wastewater, along with the hydrotreating of the bio-oil. The simulation process began with a wastewater flow rate of 460 tonnes/day, where the feedstock was divided into two streams. The first stream underwent the HTL process, while the other was directed towards hydrogen production. The resulting products included gaseous products, crude bio-oil, and heavy liquid. The crude bio-oil was further upgraded by introducing hydrogen, which was obtained through gasification and purified by gas separation using a palladium membrane. The primary product mainly comprised alkane, with a carbon content of 85.89% and hydrogen content of 14.11%. For the purification of gasoline, kerosene, diesel, and fuel oil, a fractionation distillation tower arrangement was designed. In addition, Additionally, the gaseous products underwent fractionation distillation to obtain 98% nitrogen and 99.9% liquid carbon dioxide. Considering the carbon footprint, it was observed that the bio-oil production process resulted in the highest greenhouse gas (GHG) emissions.

**Keyword.** Bio-oil, Hydrothermal liquefaction, Process design, Sewage, Upgrading

## 1 Introduction

Nowadays, daily wastewater in Thailand reaches 9.5 million cubic meters; however, the management capacity is limited to only 3 million cubic meters per day. The sewage sludge generated from industrial wastewater contributes to water pollution through odor and chemical contamination. Traditionally, sewage sludge is disposed of through landfilling and combustion. Nevertheless, there is potential to harness energy from sewage sludge through thermochemical processes like pyrolysis or liquefaction [1].

Hydrothermal liquefaction in a batch reactor typically operates at temperatures of 250-375 °C and pressure of 4-22 MPa, utilizing catalysts, such as NiMo/Al<sub>2</sub>O<sub>3</sub>, CoMo/Al<sub>2</sub>O<sub>3</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub> [2]. The resulting product is crude bio-oil with a yield of 27.5 wt% and an energy content of 40 MJ/kg [4]. The chemical components include fatty acid methyl esters, alkanes, ketones, amines, amides, and aromatic hydrocarbons [3]. Gaseous compounds like CO<sub>2</sub>, NH<sub>3</sub> and CH<sub>4</sub> are also produced. However, the crude bio-oil requires upgrading through hydrotreating processes such as hydrogenation, hydrodeoxygenation (HDO), decarboxylation (DCO<sub>2</sub>), decarbonylation (DCO) and hydrocracking. For example, bio-oil can be

hydrogenated using an H<sub>2</sub>/oil ratio of 2100 L/L, a temperature of 420 °C, and a pressure of 12.4 MPa in the presence of NiMo catalyst to enhance the bio-oil properties for its intended applications [4].

It is well-established that hydrogen plays a crucial role in the hydrotreating process. Traditionally, hydrogen is obtained from refineries or steam reforming of natural gas. However, green hydrogen production from processes, such as steam reforming of bio-oil, biomass gasification, and fermentation should be given attention [5]. A gasification process operated at a high temperature of 500-1400 °C, and a pressure of 33 bar resulted in a hydrogen yield of 25 vol.% [7]. Furthermore, integrated processes like the coupling of bio-oil upgrading with bio-oil steam reforming have been explored [6].

While literature reviews have covered bio-oil production, bio-oil upgrading, and hydrogen production. They are mostly separate processes. Moreover, the specific sources of hydrogen for bio-oil upgrading have not been mentioned. The biomass-based hydrogen was developed by pyrolysis combined with bio-oil steam reforming and biochar steam reforming [7]. Bio-oil was divided into two parts (i.e., upgrading and steam reforming for hydrogen); however, renewable resources were not mentioned [8]. Thus, this research aims to

\* Corresponding author: [lida.s@sci.kmutnb.ac.th](mailto:lida.s@sci.kmutnb.ac.th)

address this gap by proposing a combined process of bio-oil production and hydrogen production from sewage sludge, along with bio-oil upgrading. This process is developed by process simulation via Aspen Plus. The optimal conditions are determined and, the carbon footprint of the process will be evaluated to justify its worthiness.

## 2 Methodology

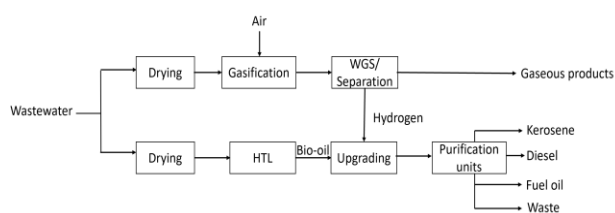
In this research, the design was based on a wastewater quantity of 460 ton/day from the Netherlands, as comprehensive data was available [9]. This quantity was divided into 2 streams: 400 ton/day for bio-oil production and 60 ton/day for hydrogen production. Material and energy balance were conducted using the Aspen Plus process simulator. Soave-Redlich-Kwong model was chosen for bio-oil production, while Peng-Robinson model was chosen for hydrogen production. The ultimate analysis and proximate analysis data are shown in Table 1. The bio-oil consisted of hydrocarbons, esters, aldehydes, ketones, and aromatic hydrocarbons. While some components were conventional, complex components were treated as pseudo-components, requiring their chemical structures to be incorporated into the program.

**Table 1.** Ultimate analysis and proximate analysis of sewage sludge in wastewater.

Ultimate analysis (wt.%)					Proximate analysis (wt.%)		
C	H	O	N	Ash	FC*	VM*	Ash
38.2	6.6	23.9	6.4	24.9	6.2	68.9	24.9

\*FC = Fixed carbon, VM = Volatile matter.

A block flow diagram of the conceptual design process was generated as shown in Figure 1. Based on the diagram, the main products are gasoline, kerosene, diesel, and fuel oil, while the by-products are nitrogen, hydrogen and dry ice. The unit model consists of pump, compressor, valve, mixer, reactor, flash separator, distillation column, heater and cooler. The reactor model of Hydrothermal liquefaction (HTL) is RYield, which sets the mass yield. The upgrading reactor is modeled using a conversion reactor, which specifies the fractional conversion. The distillation model used is Radfrac model.



**Fig. 1.** Conceptual design of the integrated process.

## 3 Process design

The integrated processes for bio-oil production, bio-oil upgrading, and hydrogen production from sewage sludge are illustrated in Figure 2. The overall process can be divided into 3 distinct sub-processes: bio-oil production process, hydrogen production process, and bio-oil upgrading process.

### 3.1 Bio-oil production process

A steady-state model for the bio-oil production process was developed and depicted in Figure 2. The wastewater underwent pressurization using a pump to achieve a pressure of 200 bar and was then heated to 350 °C. The preheated stream was directed into the HTL reactor, where the mass yield was determined. The effluent from the reactor underwent a pressure reduction via a valve and was subsequently passed through a three-phase separator to separate the gaseous products, light products, and heavy products. The gaseous products included hydrogen, nitrogen, carbon dioxide, carbon monoxide, methane, ethane, propane, butane, ammonia, and ethylene. The light product obtained is known as crude bio-oil while the heavy product is wastewater. The crude bio-oil was subjected to centrifugation when the liquid-to-solid mass ratio reached 0.103.

### 3.2 Hydrogen production process

In the hydrogen production process depicted in Figure 2, it starts with the wastewater being passed through a dryer at 1 bar and 100 °C. Then, a separator is used to remove water and sludge. The sludge is then sent to the gasification reactor. To determine the yields of water, ash, carbon, hydrogen, nitrogen, chlorine, sulfur, and oxygen, a calculator block integrated into the process simulator is utilized. The separator is used to remove the ash. The gaseous product obtained from the separator is then conveyed to the gasification reactor, which is modeled by the Gibb reactor. Finally, the effluent from the reactor is passed through a membrane [10].

### 3.3 Bio-oil upgrading process

In the bio-oil upgrade process depicted in Figure 2, the crude bio-oil obtained from bio-oil production undergoes pumping to increase the pressure to 120 bar, followed by preheating at 400 °C. The preheated stream, along with hydrogen from the hydrogen production section, is then directed to the upgrading reactor. The reactions (i.e. hydrogenation, decarboxylation, desulfurization, decarbonylation) are defined. The composition and flow rate of the products are performed after the fractional conversion of the reactions is assumed according to Table 2. Then, the product stream is sent for separation into gaseous products, an oil stream, and water. The oil stream is directed to the first distillation column to remove any remaining gaseous products before being transferred to the second distillation column for the separation of crude gasoline from crude oil. To ensure

high purity, the crude gasoline is further purified using an additional distillation column to remove ethyl diamine. Consequently, highly pure gasoline, consisting of 92 wt% hydrocarbon compounds (C6-C9), is obtained. The crude oil from the first distillation column is introduced to another distillation column for the purification of kerosene (hydrocarbon compounds C11-C14), achieving a purity of 99 wt%. The crude oil collected from the bottom of the second distillation column mainly consists of hydrocarbon compounds. Thus, it is directed to the final distillation column, resulting in the production of highly pure diesel (hydrocarbon compounds C15-C16) at the overhead column, while fuel oil (hydrocarbon compounds C17) is obtained at the bottom of the distillation column.

The gaseous products obtained from the 3-phase separator in the bio-oil production section are combined with the gaseous products from the first distillation column in the bio-oil upgrading section before entering the distillation column to eliminate waste. To purify the gaseous products, they are sent to a compressor, followed by a cooler, and then sent to the distillation column. As a result, nitrogen, with a purity of 98 wt%, is obtained, while CH<sub>4</sub> and CO are obtained in another distillation column. After removing CH<sub>4</sub> and CO, the bottom stream of the distillation column is passed through a reducing valve, cooler and the distillation column, respectively. Through this process, a high-purity CO<sub>2</sub>, with a purity of 99 wt%, is obtained.

**Table 2.** Fractional conversion of the reaction in the conversion reactor

Reaction	Fractional conversion
Formic acid → CO <sub>2</sub> + H <sub>2</sub>	1
Acetic acid → CH <sub>4</sub> + CO <sub>2</sub>	1
Glycerol + 3H <sub>2</sub> → Propane + 3 H <sub>2</sub> O	1
Phenol + 5H <sub>2</sub> → Hexane + H <sub>2</sub> O	1
Vinylcyclohexane + 2H <sub>2</sub> → Ethylcyclohexane	1
1-Ethyl-2,5-Pyrrolidinedione + 6H <sub>2</sub> → Butane + Ethylamine + 2H <sub>2</sub> O	1
2,3-Xylenol + 4H <sub>2</sub> → 1,2-Dimethylcyclohexane + H <sub>2</sub> O	1
2,6-Diethylcyclohexanone + H <sub>2</sub> → nonane + CO	1
5-Hydroxymethylfurfural + 7H <sub>2</sub> → Hexane + 3H <sub>2</sub> O	1
Hexadecanoic acid + 3H <sub>2</sub> → Hexadecane + 2H <sub>2</sub> O	0.05

Reaction	Fractional conversion
Hexadecanoic acid → Pentadecane + CO <sub>2</sub>	0.65
Hexadecanoic acid + H <sub>2</sub> → Pentadecane + H <sub>2</sub> O + CO	0.3
Tetradecanoic acid + 3H <sub>2</sub> → Tetradecane + 2H <sub>2</sub> O	0.05
Tetradecanoic acid → Tridecane + CO <sub>2</sub>	0.65
Tetradecanoic acid + H <sub>2</sub> → Tridecane + CO + H <sub>2</sub> O	0.3
Octadecanoic acid + 3H <sub>2</sub> → Octadecane + 2H <sub>2</sub> O	0.05
Octadecanoic acid → Heptadecane + CO <sub>2</sub>	0.65
Octadecanoic acid + H <sub>2</sub> → Heptadecane + CO + H <sub>2</sub> O	0.3
2-Methyl-pyrimidine + 5H <sub>2</sub> → Propane + Ethylenediamine	1
3-Hydroxy-dodecanoic acid + H <sub>2</sub> → Undecane + CO <sub>2</sub> + H <sub>2</sub> O	0.65
3-Hydroxy-dodecanoic acid + 2H <sub>2</sub> → Undecane + CO + 2H <sub>2</sub> O	0.3
3-Hydroxy-dodecanoic acid + 4H <sub>2</sub> → Dodecane + 3H <sub>2</sub> O	0.05
1-Ethyl-2-pyrrolidinone + 4H <sub>2</sub> → Butane + Ethylamine + H <sub>2</sub> O	1
Methylthiopyrrolidone → Butane + Methylamine + H <sub>2</sub> S	1
Ethylbenzene + 3H <sub>2</sub> → Ethylcyclohexane	1
5,6,7-Trimethyl-indole + 6H <sub>2</sub> → 1-Methyl-ethylcyclohexane + Ammonia	1
Tetradecanamide + H <sub>2</sub> → CO + Ammonia + Tridecane	0.9
Tetradecanamide + 3H <sub>2</sub> → H <sub>2</sub> O + Ammonia + Tetradecane	0.1
Hexadecanamide + H <sub>2</sub> → CO + Ammonia + Heptadecane	0.9
Hexadecanamide + 3H <sub>2</sub> → H <sub>2</sub> O + Ammonia + Hexadecane	0.1
Octadecanamide + H <sub>2</sub> → CO + Ammonia + Heptadecane	0.9
Octadecanamide + 3H <sub>2</sub> → H <sub>2</sub> O + Ammonia + Octadecane	0.1
Diundecyl phthalate + 7H <sub>2</sub> → 2Undecane + 2H <sub>2</sub> O + Cyclohexane + 2CO	1

Reaction	Fractional conversion
Diphenyl-1,4-phenylenediamine + 13H <sub>2</sub> → 2Ammonia + 3Cyclohexane	1
Cholesterol + 2H <sub>2</sub> → Cholestane + H <sub>2</sub> O	1

## 4 Results and Discussions

The simulation results in the bio-oil production have been validated using literature data. In the hydrogen production section, the equivalence ratio between air and sludge was determined to maximize the yield of hydrogen. In the upgrading production, the effect of design parameters of distillation columns was studied.

### 4.1 Validation of simulation results

According to the previous section, the yield of products in an HTL reactor is specified because the HTL reactions are quite complex. In addition, the literature has provided information on the mass fraction of 44 compounds. A comparison between the simulation results and the literature data is presented in Table 3, which demonstrates the accuracy of the simulation results with a low percentage deviation. However, the deviation of heptane is high. This is because the significant figures of the literature are 4. While the significant figures of the simulation are 6. In this research, 4 significant digits are reported. For the bio-oil upgrading reactor, it is assumed that 35 reactions and fractional conversion govern the percentages of C, H, O, N content. The comparison of the percentages of C, H, O, N content, as shown in Table 4, further confirms the accuracy of the simulation results, with a low percentage deviation observed.

### 4.2 Effect of equivalence ratio (ER)

In this section, the effect of the equivalence ratio in the Gibb reactor is studied by sensitivity analysis. The composition and flow rate of products are computed. Thus, the production yields from literatures are not required. Figure 3 illustrates the relationship between gas yields of H<sub>2</sub>, CO and CO<sub>2</sub> and the equivalence ratio, which represents the ratio of wastewater to air. The temperature of the Gibb reactor is fixed at 620 °C. The possible reactions in the Gibb reactor include reforming, cracking, and combustion. Hydrogen is formed by reforming and cracking, while CO and CO<sub>2</sub> are formed by combustion of fuel. However, the ER ratio should not be too high due to the increased formation of CO<sub>2</sub>. Thus, the optimal ER ratio is crucial. Considering an air flow rate of 2500 kmol/h, the maximum yield of H<sub>2</sub> amounts to 76.8 kg/h (82.8 kmol/h). Subsequently, the gaseous product mixture is sent to the membrane to purify and produce hydrogen of 99 wt% [8]. The hydrogen yield after purification is 76.05 kg/h.

**Table 3.** The comparison of composition in HTL reactor between literatures and simulation results

Composition	Mass fraction		
	Reported literature	Simulation	% deviation
Water	0.8466	0.8465	0.01181
Hydrogen	0.0000	1.466×10 <sup>-5</sup>	1.466×10 <sup>-5</sup>
Nitrogen	0.0001	1.085×10 <sup>-4</sup>	0
Carbon dioxide	0.0285	0.0285	0
Carbon monoxide	0.0002	2.082×10 <sup>-4</sup>	0
Methane	0.0003	3.108×10 <sup>-4</sup>	0
Ethane	0.0002	1.525×10 <sup>-4</sup>	0
Ammonia	0.0084	8.372×10 <sup>-3</sup>	0
Ethylene	0.0001	8.907×10 <sup>-5</sup>	10.93
Propane	0.0002	2.672×10 <sup>-4</sup>	0
n-Butane	0.0010	9.797×10 <sup>-4</sup>	2.030
Formic acid	0.0087	8.729×10 <sup>-3</sup>	0.3333
Acetic acid	0.0022	2.226×10 <sup>-3</sup>	0.9090
Glycerol	0.0015	1.425×10 <sup>-3</sup>	5
Phenol	0.0014	1.389×10 <sup>-3</sup>	0.7857
Vinyl cyclohexene	0.0002	1.998×10 <sup>-4</sup>	0.055
o-Cresol	0	0	0
p-Cresol	0	0	0
2,5-Pyrrolidinedione, 1-ethyl-	0.0001	7.196×10 <sup>-5</sup>	28.04
2,3-Xylenol	0.0004	3.678×10 <sup>-4</sup>	8.25
Cyclohexanone, 2,6-diethyl-	0.0000	7.995×10 <sup>-6</sup>	7.995×10 <sup>-6</sup>
n-Hexane	0.0000	2.398×10 <sup>-5</sup>	2.398×10 <sup>-5</sup>

Composition	Mass fraction		
	Reported literature	Simulation	% deviation
n-Heptane	0.0001	$1.439 \times 10^{-4}$	43.9
n-Octane	0.0000	$7.995 \times 10^{-6}$	$7.995 \times 10^{-6}$
5-Hydroxymethylfurfural	0.0012	$1.175 \times 10^{-3}$	2.051
n-Hexadecanoic acid	0.0048	$4.813 \times 10^{-3}$	0.2708
n-Tetradecanoic acid	0.0036	$3.622 \times 10^{-3}$	0.6111
Stearic acid	0.0076	$7.603 \times 10^{-3}$	0.0394
Pyrimidine, 2-methyl-	0.0188	$1.879 \times 10^{-2}$	0.0218
Dodecanoic acid, 3-hydroxy-	0.0015	$1.514 \times 10^{-3}$	0.9480
1-Ethyl-2-Pyrrolidinone	0.0011	$1.108 \times 10^{-3}$	0.7272
n-Methylthiopyrrolidone	0.0019	$1.959 \times 10^{-3}$	2.6315
Ethylbenzene	0.0001	$1.199 \times 10^{-4}$	10
p-EthylPhenol	0	0	0
Indole	0	0	0
7-Methylindole	0.0088	$8.803 \times 10^{-3}$	0.0340
Myristic amide	0.0049	$4.861 \times 10^{-3}$	0.8163
Palmitic acid amide [Hexadecanamide]	0.0096	$9.554 \times 10^{-3}$	0.4697
Octadecamide	0.0082	$8.203 \times 10^{-3}$	0.0365
n-Hexadecanoic acid	0.0030	$2.966 \times 10^{-3}$	1.3333
Naphthalene	0.0008	$7.995 \times 10^{-4}$	0.1250
$\beta$ -Cholesterol	0.0166	$1.655 \times 10^{-2}$	0.3012
N,N'-Diphenyl-p-phenylenediamine	0.0072	$7.236 \times 10^{-3}$	0.4167
Di-n-Undecyl-Phthalate	0.0001	$1 \times 10^{-4}$	0

### 4.3 Effect of design parameters of distillation column of the liquid products

The purification section comprises 10 distillation columns. Although flash separation effectively removes a significant portion of gaseous products, some residual gases remain due to the presence of numerous components. The first distillation column (B21) employs three stages to ensure the complete removal of gases, employing a reflux ratio of 0.06. Key components targeted for separation in this column are butane and hexane. Components with lower boiling points than butane are removed overhead, resulting in gaseous products such as carbon dioxide, ammonia, methane, ethylene, propane, butane, hydrogen sulfide and ethylamine.

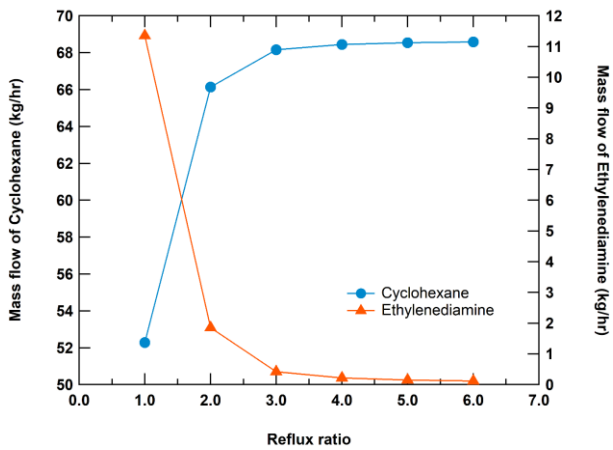
The remaining distillation columns are designed to separate key components based on the fuel type, taking into account their respective quantities and boiling points. For instance, distillation column B25 is dedicated to gasoline separation. Thus, 1-methyl-ethylcyclohexane is represented as a light key component while undecane is a heavy key component. In distillation column B27, cyclohexane is the designated light key component, while ethylenediamine is the heavy key component. The distillation column B33 focuses on kerosene separation, with kerosene itself acting as the light key component, while hydrocarbon compounds above C15 serve as the heavy key component. Finally, the distillation column B35 is employed for the purification of diesel and fuel oil. Diesel is considered the light key component in this column, while fuel oil takes the role of the heavy key component. The effect of various parameters such as the number of stages, reflux ratio, and distillation conditions on all distillation columns is investigated.

The effect of the number of stages on the purity of gasoline is shown in Figure 4. It can be seen that the specification of gasoline is not achieved with 20 stages. The presence of ethylenediamine in the gasoline mixture results in a lower high heating value. To solve this issue, the distillation columns B27 and B30 are used. It was found that the distillation column B27 effectively removes ethylenediamine from the gasoline stream.

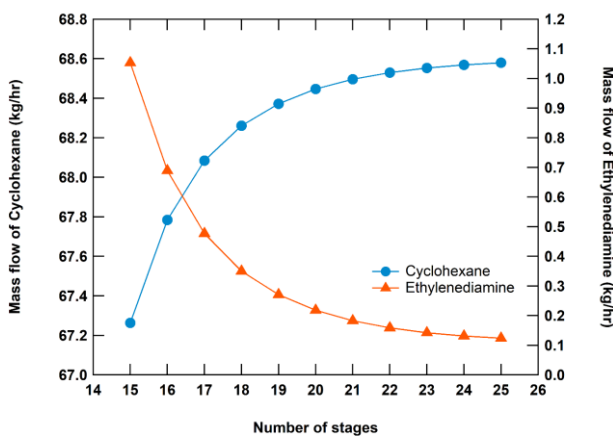
**Table 4.** The comparison of composition in bio-oil upgrading reactor between literatures and simulation results

%wt	Literature	Simulation	% deviation
C	86.1	85.89	0.22
H	13.89	14.11	C
O	0	0	0
N	0	0	0





**Fig. 6.** Effect of reflux ratio of the distillation (B27)

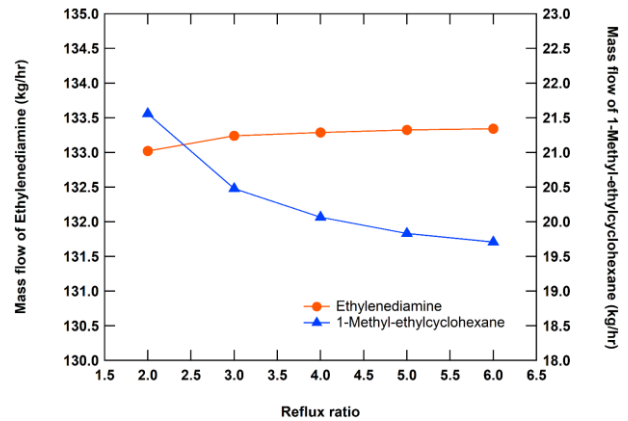


**Fig. 7.** Effect of the numbers of stages of the distillation (B27)

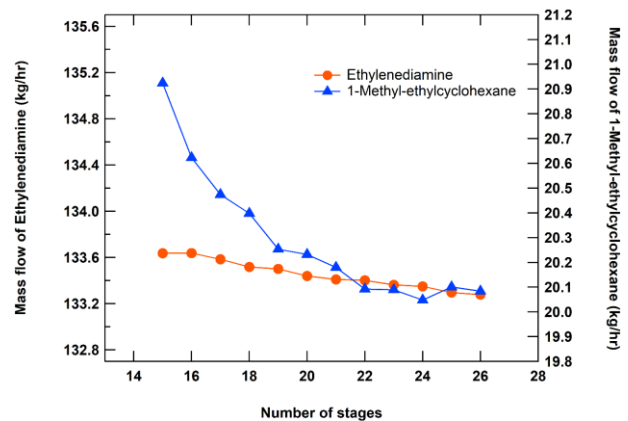
Figure 8 shows that 1-methyl-ethyl cyclohexane is separated at the bottom of the column as the reflux ratio increases. However, an increase in the reflux ratio also raises the reboiler heat duty. Hence, the reflux ratio of 3 is chosen when the number of stages is 25 stages. Increasing of the number of stages can decrease mole flow of 1-methyl, ethyl cyclohexane at the top of the column as shown in Figure 9. This implies that the distillation (B30) can separate ethylenediamine. Finally, the purified gasoline is a combination of the overhead stream from the distillation column (B27) and the bottom of the distillation column (B30). The quantity of gasoline obtained is 205.07 kg/h. This gasoline meets the product specification in terms of specific gravity, which is 0.7813. However, the simulated gasoline has a higher flash point (-10°C) compared to standard gasoline (-43°C). This is due to the presence of additional components, such as aromatic hydrocarbons, in standard gasoline.

The distillation column (B33) is responsible for purifying kerosene. The reflux ratio and number of stages play crucial roles in achieving the desired purity of kerosene. By increasing the reflux ratio, the purity of kerosene can meet the specification. As a result, kerosene can be collected at the top of the column, while diesel and fuel oil are obtained from the bottom. Figure

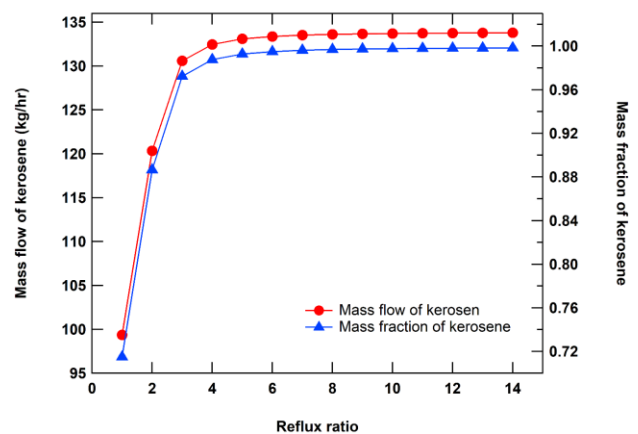
10 demonstrates that a reflux ratio of 5 yields a mass fraction of kerosene of 0.99. Moreover, an increase in the number of stages enhances the mole flow and mass fraction of kerosene at the top of the column, as depicted in Figure 11. The quantity of kerosene produced is 134.08 kg/h. The specific gravity of the simulated kerosene is 0.7832, slightly lower than the standard kerosene's specific gravity of 0.79. This variation arises from the presence of paraffins and cycloalkanes in this work's kerosene, while the standard kerosene typically contains paraffins and aromatic hydrocarbons.



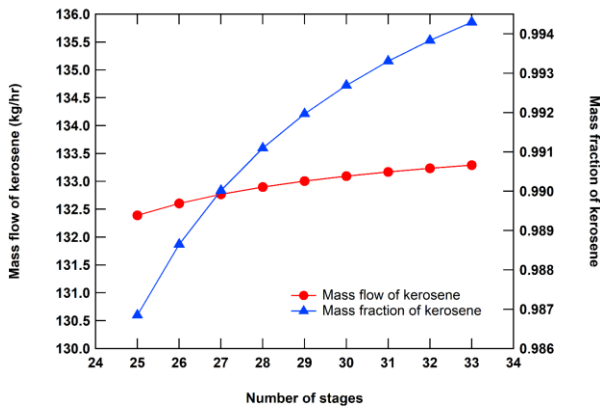
**Fig. 8.** Effect of reflux ratio of the distillation (B30)



**Fig. 9.** Effect of number of stages of the distillation (B30)

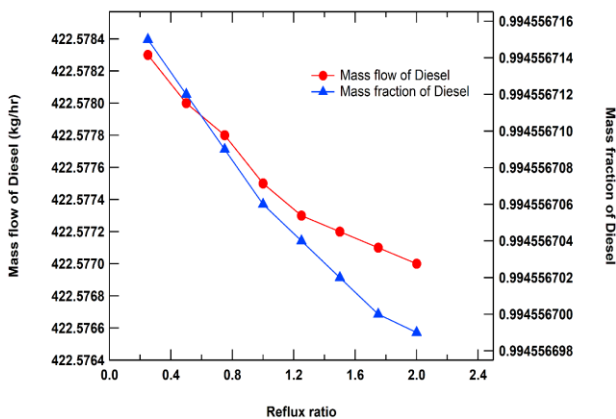


**Fig. 10.** Effect of reflux ratio of the distillation (B33)

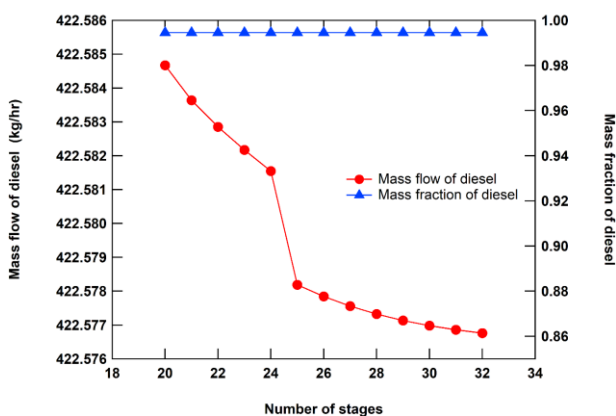


**Fig. 11.** Effect of number of stages of the distillation (B33)

The distillation column (B35) effectively separates diesel from fuel oil. The mole flow and mass fraction of diesel remain unchanged with varying reflux ratios, so a fixed reflux ratio of 0.5 is chosen. On the other hand, the number of stages plays a crucial role, as illustrated in Figure 12. Optimal performance is achieved with 30 stages, ensuring that both diesel (with a mass fraction of 0.99) and fuel oil (with a mass fraction of 0.99) meet the specification, as depicted in Figure 13. The quantity of diesel obtained is 424.899 kg/h, while the amount of fuel oil is 242.496 kg/h.



**Fig. 12.** Effect of reflux ratio of the distillation (B35)



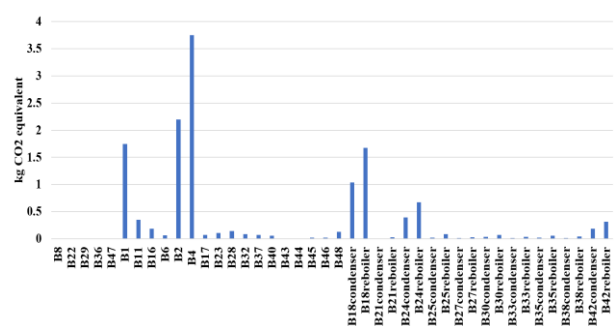
**Fig. 13.** Effect of number of stages of the distillation (B35)

In terms of the purification sequence for gaseous products, a direct sequence of distillation columns is employed. The first distillation column (B18) is utilized to remove waste gases such as Ethylenediamine, Cyclohexane, Cis-1-Methyl-3-Ethylcyclohexane, Methyl amine, Ethylamine, and hexane. Subsequently, the distillation columns (B24), (B38), and (B42) are arranged to further purify the gaseous products. The resulting sequence involves the separation of nitrogen as the first product, followed by the mixture of methane and carbon monoxide, and finally carbon dioxide. These gaseous products can attain a high purity level of 0.99 wt%. The specific impact of the distillation column parameters is not discussed in this work.

#### 4.4 Carbon footprint

In this work, the carbon footprint refers to the total greenhouse gas (GHG) emissions generated by the activities in the process. The unit of measurement used is kg CO<sub>2</sub> equivalent, which provides a metric measure for comparing different greenhouse gas emissions. The emissions are caused by heating, cooling, and pumping, which involve various heat and cooling sources. Specifically, the heating process utilizes natural gas combustion in industrial equipment, while cooling requires chill water.

Figure 14 illustrates that certain unit operations contribute to GHG emissions, particularly the heater (B4), the cooler (B2), and the HTL reactor (B1). This indicates that the bio-oil production process through hydrothermal liquefaction (HTL) results in higher GHG emissions compared to the hydrogen production process and the upgrading process. The elevated emissions can be attributed to the high operating temperature of 350 °C and the high operating pressure of 200 bar associated with the HTL reactor.



**Fig. 14.** GHG emissions contributed by unit operations

## 5 Conclusion

This work proposed an integrated process for bio-oil production and hydrogen production using sewage sludge from wastewater. The bio-oil is further upgraded through hydrogenation processes, utilizing hydrogen obtained from the hydrogen production stage. The performance analysis highlights the significance of the distillation arrangement in the separation process. This



integrated process serves as a preliminary guideline for wastewater pretreatment and enables the production of various fuel oil types, including gasoline, kerosene, diesel, and fuel oil. Furthermore, the process generates gaseous byproducts such as nitrogen gas with a purity of 99% and liquid carbon dioxide with a purity of 99%. It is important to note that the bio-oil production process exhibits the highest greenhouse gas (GHG) emissions compared to the hydrogen production and upgrading processes. However, the adverse environmental impact can be mitigated through the design of a heat exchanger network.

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