

## Article

# Improving Biomethanol Synthesis via the Addition of Extra Hydrogen to Biohydrogen Using a Reverse Water–Gas Shift Reaction Compared with Direct Methanol Synthesis

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**Abstract:** Conventionally, methanol is derived from a petroleum base and natural gas, but biomethanol is obtained from biobased sources, which can provide a good alternative for commercial methanol synthesis. The fermentation of molasses to produce biomethanol via the production of biohydrogen (H<sub>2</sub> and CO<sub>2</sub>) was studied. Molasses concentrations of 20, 30, or 40 g/L with the addition of 0, 0.01, or 0.1 g/L of trace elements (TEs) (NiCl<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O) were investigated, and the proper conditions were a 30 g/L molasses solution combined with 0.01 g/L of TEs. H<sub>2</sub>/CO<sub>2</sub> ratios of 50/50% (v/v), 60/40% (v/v), and 70/30% (v/v) with a constant feed rate of 60 g/h for CO<sub>2</sub> conversion via methanol synthesis (MS) and the reverse water–gas shift (RWGS) reaction were studied. MS at temperatures of 170, 200, and 230 °C with a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst and pressure of 40 barg was studied. Increasing the H<sub>2</sub>/CO<sub>2</sub> ratio increased the maximum methanol product rate, and the maximum H<sub>2</sub>/CO<sub>2</sub> ratio of 70/30% (v/v) resulted in methanol production rates of 13.15, 17.81, and 14.15 g/h, respectively. The optimum temperature and methanol purity were 200 °C and 62.9% (wt). The RWGS was studied at temperatures ranging from 150 to 550 °C at atm pressure with the same catalyst and feed. Increasing the temperature supported CO generation, which remained unchanged at 21 to 23% at 500 to 550 °C. For direct methanol synthesis (DMS), there was an initial methanol synthesis (MS) reaction followed by a second methanol synthesis (MS) reaction, and for indirect methanol synthesis (IMS), there was a reverse water–gas shift (RWGS) reaction followed by methanol synthesis (MS). For pathway 1, DMS (1st MS + 2nd MS), and pathway 2, IMS (1st RWGS + 2nd MS), the same optimal H<sub>2</sub>/CO<sub>2</sub> ratio at 60/40% (v/v) or 1.49/1 (mole ratio) was determined, and methanol production rates of 1.04 (0.033) and 1.0111 (0.032) g/min (mol/min), methanol purities of 75.91% (wt) and 97.98% (wt), and CO<sub>2</sub> consumptions of 27.32% and 57.25%, respectively, were achieved.

**Keywords:** biohydrogen; biomethanol; catalytic conversion; molasses fermentation; reverse water–gas shift



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## 1. Introduction

Biofuels have begun to replace fossil fuels due to their potential to reduce greenhouse gas emissions by replacing fossil fuels. Biofuels thereby have the potential to both decrease CO<sub>2</sub> emissions and increase energy security [1]. The first example is biodiesel (derived from the transesterification/esterification of vegetable oil), which is mixed with diesel fuel. The second example is biogas (derived from the decomposition of organic/agricultural waste), which generates methane (CH<sub>4</sub>), which has been used as a replacement for natural gas in the generation of heat and electricity and in vehicles. Bioethanol (produced via

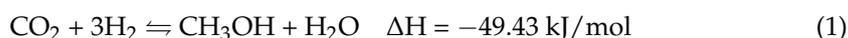
the fermentation of sugar and starch feedstocks) has been used for over three decades because it can be blended with gasoline. It is more prevalent than biomethanol due to the compatibility of bioethanol/gasoline blends with current internal combustion engines. However, biomethanol is methanol which is obtained from bio-sources such as biogas and biohydrogen, and it can also be produced from CO<sub>2</sub>. Therefore, it may be more desirable in the future and replace bioethanol due to the CO<sub>2</sub> utilization potential [2]; higher specific energy yield, which can be explained by the fact that oxygenated fuels have a better combustion efficiency and more enrichment of oxygen than ethanol, owing to methanol [3]; and high volumetric energy density [4]. Accordingly, biomethanol is easy to store and transport and can be readily used as a raw material for synthesizing a variety of useful organic compounds of industrial importance. Methanol is a valued chemical, and it can be used in various sectors as a solvent and in biodiesel, biofuels, and additives [5]. Regarding its direct usage, methanol is used as a solvent and raw material by reacting it with vegetable oil to produce biodiesel. Regarding its indirect usage, methanol is transformed into other chemicals such as formaldehyde, methyl tertiary butyl ether (MTBE)/TAME (a blending component of gasoline), dimethyl ether (DME), MTO (methanol-olefin), and MTP (methanol-paraffin). Biogas and biohydrogen derived from molasses play important roles as raw gases for biomethanol production. Biogas normally contains methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and varied amounts of hydrogen sulfide (H<sub>2</sub>S) depending on the variety of raw materials. Therefore, when using biogas as a raw material for biomethanol, it is necessary to remove H<sub>2</sub>S via a H<sub>2</sub>S separation process [6], whereas biohydrogen comprises only hydrogen (H<sub>2</sub>) and CO<sub>2</sub>. For this reason, when using biohydrogen as a raw material for biomethanol production, a H<sub>2</sub>S separation unit is not needed (saving costs), and the method is attractive due to not only reducing the CO<sub>2</sub> problem by using biohydrogen but also increasing the use of molasses to produce biohydrogen. Furthermore, this will provide another option for the sugar industry to extract value from the by-product of molasses by making biohydrogen, representing an alternative source of raw materials for biomethanol production. The industrial-scale production of methanol via thermo-chemical processes has been achieved using petroleum sources, but there is awareness that this releases CO<sub>2</sub> into the environment. On the other hand, the implementation of the biological conversion process at the laboratory scale is still being investigated and lacks sufficient information. The biochemical production of methanol requires the microbes and metabolic pathways and enzymes that are involved to be studied to properly understand the bioconversion process and determine the essential parameters for scaling up the laboratory process to full-size production units. Integrating these biological and thermo-chemical processes could provide an opportunity to make the production of biomethanol feasible.

Agricultural/organic wastes, such as manure, feed, fruit, cassava, bagasse, and molasses, are abundant resources that can be turned into biofuels. Molasses is a plentiful resource obtained from sugar production and is used to produce fermented ethanol, which has been promoted for blending with gasoline [7]. Electric vehicles are becoming a substitute for vehicles that require the use of fossil fuels for power, especially gasoline vehicles, which normally use ethanol-blended gasoline. As a result, increased electric vehicle usage will lead to a reduction in ethanol production. Ethanol production will be disrupted and decreased due to decreasing demand, which means that the demand for molasses as a raw material will be reduced, affecting the income of sugarcane farmers. To compensate for this situation, transforming molasses into hydrogen via the fermentation process is desirable as it only generates H<sub>2</sub>, i.e., biohydrogen, and CO<sub>2</sub> [8,9]. Hydrogen can be used in hydrogen fuel cells, for the hydrogen treatment of biodiesel/vegetable oil to produce bio-oleochemicals, and to transform carbon dioxide into an important precursor to petrochemicals, such as methane or methanol [10,11].

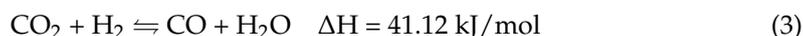
Conventionally, methanol production requires a mixture of synthesis gases (H<sub>2</sub>, CO, and CO<sub>2</sub>) that is obtained from the steam reforming of natural gas (CH<sub>4</sub> and CO<sub>2</sub>). In the case of using a biohydrogen source (H<sub>2</sub> and CO<sub>2</sub>) for producing biomethanol, direct methanol synthesis (DMS) can be performed, which is the reaction of CO<sub>2</sub> and H<sub>2</sub> using

an appropriate catalyst, specific temperature, and pressure, resulting in methanol and water as the products, following Equation (1). However, CO<sub>2</sub> and H<sub>2</sub> can be reacted through a reverse water–gas shift (RWGS) reaction, obtaining CO and H<sub>2</sub>O, following Equation (3). An advantage of RWGS is that it can be applied for transforming CO<sub>2</sub> and H<sub>2</sub> into CO and H<sub>2</sub>O as products, meaning that the H<sub>2</sub>O liquid can be easily separated, and then CO will react with the excess H<sub>2</sub>, following Equation (2), which is called indirect methanol synthesis (IMS), resulting in methanol as a product; this methanol is purer than that obtained from the reaction shown in Equation (1). However, there is a side reaction called a water–gas shift (WGS), shown in Equation (4), which is the reverse reaction of RWGS [3,12–14]. Biohydrogen sources (H<sub>2</sub> and CO<sub>2</sub>) can be used as raw materials for producing methanol.

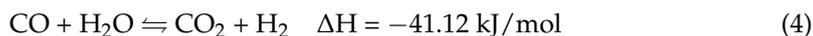
Methanol synthesis (MS)



Reverse water–gas shift (RWGS)



Water–gas shift (WGS)



The purpose of this article is to guide the optimization of biohydrogen in terms of the molasses concentration and the concentration of trace elements. The transformation of biohydrogen into biomethanol was studied. The effect of the H<sub>2</sub>/CO<sub>2</sub> ratio on CO<sub>2</sub> hydrogenation and the RWGS was investigated. Two pathways for transforming biohydrogen and CO<sub>2</sub> were investigated, and both pathways involved a two-step reaction: pathway 1 included two-step methanol synthesis involving direct CO<sub>2</sub> hydrogenation (Equation (1)) comprising a first methanol synthesis (1st MS) and second methanol synthesis (2nd MS), with both steps connected in a series fixed-bed reactor operated using the same catalyst and controlled temperature, as shown in the Materials and Methods section; pathway 2 was an innovative route comprising a reverse water–gas shift (RWGS) as shown in Equation (3) and then methanol synthesis (MS) as shown in Equation (2). The same catalyst was used for each step, but each step had a different temperature and pressure, as described in the Materials and Methods section. The methanol production rate, methanol purity, and CO<sub>2</sub> consumption were obtained for both pathways.

## 2. Materials and Methods

### 2.1. Biohydrogen Experiment

#### 2.1.1. Microorganism, Culture Conditions, and Raw Materials

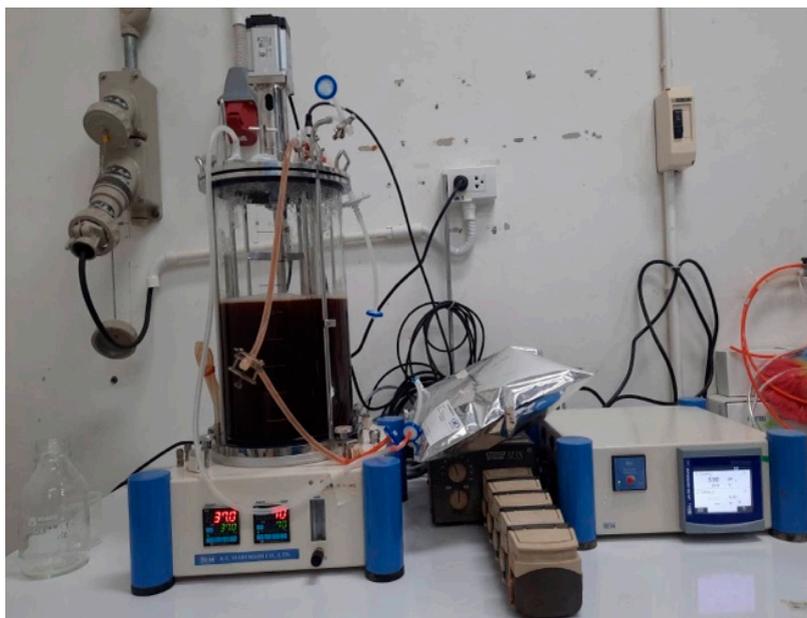
- The bacterial strain *Enterobacter aerogenes* (E.A.) (TISTR 1540) was obtained from the Biodiversity Research Center of the Thailand Institute of Scientific and Technological Research (TISTR), maintained at 0 °C with 15% purified glycerol, and used for H<sub>2</sub> production from molasses.
- Molasses obtained from the Konkaen sugar company was dissolved in deionized water at concentrations of 20, 30, and 40 g/L.
- The following nutrient medium was prepared: beef extract (1.0 g/L), yeast extract (2.0 g/L), peptone (5.0 g/L), and NaCl (5.0 g/L). This was then placed in deionized water and sterilized in an autoclave for 15 min at 121 °C. After that, the bacteria were incubated in the nutrient medium for 18 h.
- The synthetic medium contained the following components: (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (4.0 g/L), KH<sub>2</sub>PO<sub>4</sub> (5.5 g/L), tryptone (5 g/L), yeast extract (5 g/L), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (1g/L), MgSO<sub>4</sub>·7H<sub>2</sub>O

(0.25g/L),  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (0.020g/L), and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (0.12g/L). The trace elements were  $\text{NiCl}_2$  (0.01 and 0.1 g/L) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (0.01 and 0.1 g/L).

- $\text{N}_2$  gas and gas mixtures of  $\text{CO}_2$  and  $\text{H}_2$  were supplied by the Thai Special Gas Company.

### 2.1.2. Apparatus and Operation

- A 10 L bioreactor with a 5 L working volume was used in the biohydrogen experiment and obtained from Marubishi (model: MDFT-10 L), as shown in Figure 1.



**Figure 1.** Ten-liter bioreactor for biohydrogen production.

- The fermentation conditions were a 37 °C temperature, agitation by rotation at 70 rpm, and a pH of 6.0–7.0.
- Molasses solutions (20, 30, and 40 g/L) were prepared and dissolved in solutions of a medium with a volume of 5L containing different quantities of trace elements (0, 0.01, and 0.1 g); the pHs were adjusted to 7.0 and then the solutions were sterilized (for 15 min at 121 °C) in an autoclave.
- After removal from the autoclave, the solutions were cooled and then 10% of each seed culture was inoculated into the bioreactor.
- To prepare the limited aerobic conditions, nitrogen ( $\text{N}_2$ ) was used to purge the bioreactor until the oxygen ( $\text{O}_2$ ) was detected to be below 1%, the temperature was set at 37 °C, and the contents were agitated at 70 rpm. The gas product was collected using an aluminum gas bag and a sample was taken every 6 h. The fermentation time was 72 h, continually, per batch.

## 2.2. Biomethanol Experiment

### 2.2.1. Raw Materials

- The commercial catalyst  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  was supplied by Xi'an Sunward Aeromat Co., Ltd., Xi'an, China. An amount of 5 kg of the catalyst was placed in reactor 1 (RX1) and in reactor 2 (RX2). The activation conditions for the catalyst were feeding 15%  $\text{H}_2$  mixed with  $\text{N}_2$  at a temperature of 230 °C and pressure of 3 barg for 18 h.
- The raw gas composition ( $\text{H}_2$  and  $\text{CO}_2$ ) obtained using the biohydrogen reactor was measured using an Agilent gas chromatograph (model: 7890 B).
- The gas compositions in the feeds and products of the biomethanol synthesis and reverse water–gas shift experiments were measured using a gas analyzer (MRU model,

Vario luxx), as shown in Figure 2, which measured the gas compositions ( $H_2$ ,  $CO$ ,  $CO_2$ ,  $O_2$ ,  $N_2$ , and  $CH_4$ ) in % by volume, and the sum of the gases was 100% by volume.



Figure 2. Gas analyzer (MRU model, Vario luxx).

### 2.2.2. Apparatus and Operation

- Reactor 1 (RX1) and reactor 2 (RX2) were identical fixed-bed reactors used for the biomethanol synthesis experiments. The fixed-bed reactors had an inside diameter of 16 cm and a length of 30 cm, were made from 304 stainless steel, and were filled with 5 kg of  $Cu/ZnO/Al_2O_3$ . Each heater was used to supply heat to each reactor with a program controlling the temperature from 30 to 600 °C.
- Mass flow controllers were used to control all the gases feeding the reactors: mass flow of biohydrogen (MFBH), mass flow of hydrogen (MFH), mass flow of carbon dioxide (MFC), mass flow of nitrogen (MFN), and mass flow of syngas (MFSG).
- Other equipment: cool separator 1 (CS1) was used to separate the liquid product from the gas product from RX1. Cool separator 2 (CS2) was used to separate the liquid product from the gas product from RX2. A low-pressure tank (LPT) was used to collect the gas product from CS1. A compressor was used to build up and compress the low-pressure gas to obtain high-pressure gas and then it was stored in a high-pressure tank (HPT). Cool water from a chiller was supplied to CS1 and CS2 for liquid–gas separation.

The two-step biomethanol synthesis (TSBS) process was set up with two identical fixed-bed reactors (RX1 and RX2) connected in series and linked with all the apparatus, as shown in Figure 3. It was used for the biomethanol synthesis experiments described in Sections 3.2–3.4 (note that Section 3.1 describes the biohydrogen experiment).

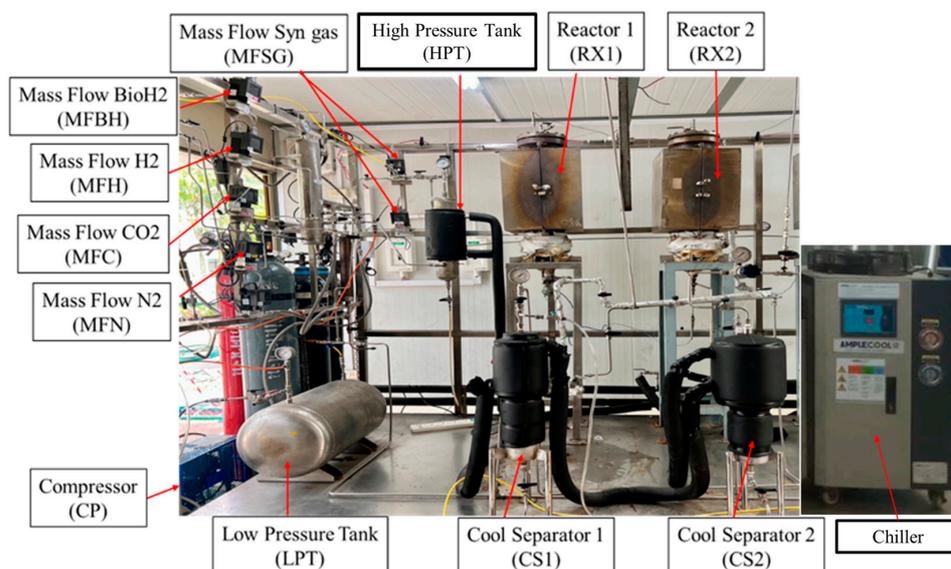


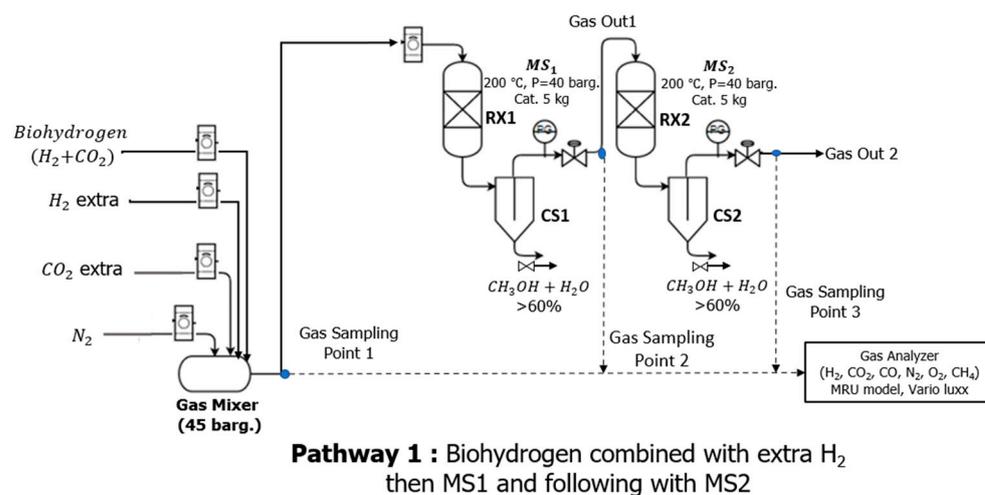
Figure 3. Two-step methanol synthesis process.

Section 3.2: In this experiment, direct CO<sub>2</sub> hydrogenation using RX2 only was studied.

Section 3.3: In this experiment, the transformation of CO<sub>2</sub> into CO via the RWGS reaction using RX1 only was studied.

Section 3.4: In this experiment, the transformation of biohydrogen into biomethanol via pathway 1—direct methanol synthesis (DMS) + direct methanol synthesis (DMS) (1st MS + 2nd MS)—and pathway 2—indirect methanol synthesis (IMS) comprised of RWGS + direct methanol synthesis (DMS) (1st RWGS + 2nd MS)—was studied.

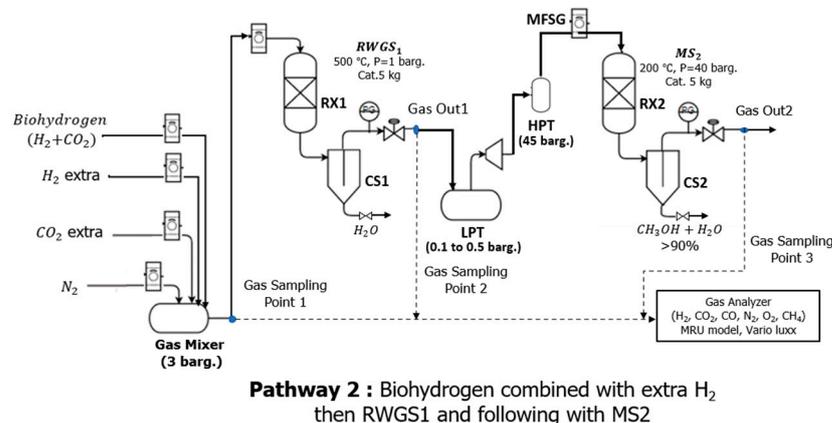
Pathway 1: The process diagram for DMS+DMS, methanol synthesis reaction step 1 (1st MS), and methanol synthesis reaction step 2 (2nd MS) is shown in Figure 4. The experiment was started by feeding a gas comprising biohydrogen (H<sub>2</sub> + CO<sub>2</sub>) using MFBH and the gas composition was adjusted with CO<sub>2</sub> or H<sub>2</sub> using MFC or MFH; then, all the gases were blended in a gas mixer until the following volume ratios of H<sub>2</sub>/CO<sub>2</sub> were obtained: 50/50% (v/v), 60/40% (v/v), and 70/30% (v/v). The gas was transferred by MFSG to reactor 1 (RX1), in which the temperature was controlled at 200 °C and the pressure was controlled at 40 barg. After the reaction, hot fluid flowed out of the first reactor and cooled down in CS1 and then the liquid was removed by opening the bottom valve connected to CS1. Gas flowed out from the top of CS1 and was fed continuously into reactor 2 (RX2), in which the temperature was controlled at 200 °C and the pressure was controlled at 40 barg for methanol synthesis. After the reaction in RX2, the fluid was cooled in CS2. The liquid was removed from the bottom of CS2 and the gas was extracted. The compositions of the gases were measured using a gas analyzer, MRU, which was connected in three positions, as shown in Figure 4.



**Figure 4.** Process flow diagram of the H<sub>2</sub>/CO<sub>2</sub> experiment via pathway 1: MS1 and MS2 in fixed-bed reactor.

Pathway 2: The process diagram of IMS + DMS, the reverse water–gas shift reaction (RWGS), and methanol synthesis reaction (MS) were carried out as shown in Figure 5. The experiment was started using a set-up pressure of 3 barg for all the feeding gases, which comprised biohydrogen (H<sub>2</sub> + CO<sub>2</sub>), which was fed by MFBH, and the gas composition was adjusted using CO<sub>2</sub> or H<sub>2</sub> by MFC or MFH; then, all the gases were blended in a gas mixer until the following volume ratios of H<sub>2</sub>/CO<sub>2</sub> were obtained: 50/50% (v/v), 60/40% (v/v), and 70/30% (v/v). The gas was sent by MFSG to reactor 1 (RX1), in which the temperature was controlled at 500 °C and the pressure was controlled at atmospheric pressure. After the reaction, hot fluid flowed out of the first reactor and cooled down in CS1 and then the liquid was removed by opening the bottom valve connected to CS1. Gas flowed out from the top of CS1 and was collected in LPT, and the minimum and maximum pressures were controlled at 0.1 and 0.5 barg, respectively. The compressor (CP) started to compress the gas into HPT when the gas pressure in the LPT reached the maximum pressure and stopped when the minimum pressure was reached. The gas was collected in the HPT until

the pressure reached over 45 barg and was prepared to be fed continuously with MFSG into reactor 2 (RX2), the pressure in which was controlled at 40 barg by a gas back-pressure regulator. After the reaction in RX2, the fluid was cooled in CS2. The liquid was removed from the bottom of CS2 and the gas was drawn out. The compositions of the gases were measured using a gas analyzer, MRU, which was connected in three positions, as shown in Figure 5.



**Figure 5.** Process flow diagram of the H<sub>2</sub>/CO<sub>2</sub> experiment via pathway 2: RWGS1 and MS2 in fixed-bed reactor.

### 3. Results

#### 3.1. Optimization of Biohydrogen with Varying Molasses Concentrations versus Trace Element (TE) Concentrations with *Enterobacter Aerogenes*

The production of biohydrogen was studied by investigating two parameters: the molasses concentration (MC) and the trace element (TE) concentration. The experiments were performed by comparing molasses concentrations of 20, 30, and 40 g/L corresponding to low, medium, and high levels, respectively, and then combining them with the two metal sources of NiCl<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O (TEs) at varying concentrations of 0, 0.01, 0.05, and 0.1 g/L, as shown in Table 1.

**Table 1.** Biohydrogen experimental conditions.

No.	Conditions	Total Gas (L)			H <sub>2</sub> /CO <sub>2</sub>		
		1st Batch	2nd Batch	Ave.	1st Batch	2nd Batch	Ave.
1.	20 g/L Mol. <sup>2</sup> , 5 g/L Try <sup>3</sup> , TE <sup>1</sup> not added	10.50	9.50	10.00	0.37	0.33	0.35
2.	20 g/L Mol., 5 g/L Try, 0.01 g/L TE	10.00	11.00	10.50	1.01	1.05	1.03
3.	20 g/L Mol., 5 g/L Try, 0.05 g/L TE	9.87	10.59	10.23	0.36	0.32	0.34
4.	20 g/L Mol., 5 g/L Try, 0.10 g/L TE	9.20	9.82	9.51	0.29	0.25	0.27
5.	30 g/L Mol., 5 g/L Try, TE not added	14.01	14.67	14.34	0.43	0.41	0.42
6.	30 g/L Mol., 5 g/L Try, 0.01 g/L TE	31.00	31.72	31.36	0.99	0.95	0.97
7.	30 g/L Mol., 5 g/L Try, 0.05 g/L TE	20.48	21.32	20.90	0.35	0.41	0.38
8.	30 g/L Mol., 5 g/L Try, 0.10 g/L TE	11.50	9.38	10.44	0.32	0.3	0.31
9.	40 g/L Mol., 5 g/L Try, TE not added	11.60	13.70	12.65	0.53	0.49	0.51
10.	40 g/L Mol., 5 g/L Try, 0.01 g/L TE	26.70	27.14	26.92	0.51	0.49	0.50
11.	40 g/L Mol., 5 g/L Try, 0.05 g/L TE	17.12	16.68	16.90	0.50	0.5	0.50
12.	40 g/L Mol., 5 g/L Try, 0.10 g/L TE	6.30	7.46	6.88	0.52	0.48	0.50

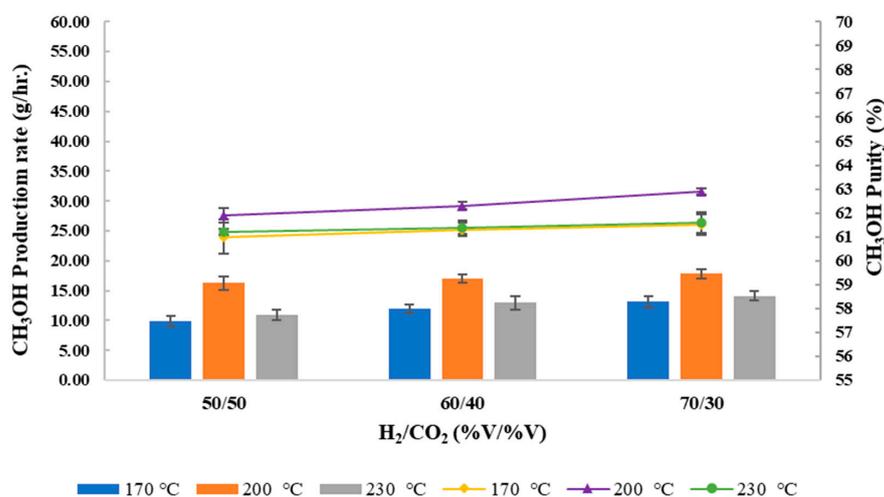
<sup>1</sup> TE = trace element, <sup>2</sup> Mol. = molasses, <sup>3</sup> Try = tryptone.

The results show that the molasses concentration affected biohydrogen generation. It was found that using 30 g/L of molasses resulted in the best biohydrogen generation, better than molasses concentrations of 20 and 40 g/L, for every concentration of TEs added. Increasing the TE concentration in the system from 0, 0.01, 0.05, and 0.1 g/L demonstrated

that 0.01 g/L of TEs enhanced both the maximum biohydrogen and the H<sub>2</sub>/CO<sub>2</sub> ratio. As shown in Table 1, the optimal combination was a 30 g/L molasses concentration and 0.01 g/L TE concentration, which produced 31.36 L of biohydrogen and a 0.97 H<sub>2</sub>/CO<sub>2</sub> mole ratio. Implementing a TE concentration above this did not increase biohydrogen production at any molasses concentration because TE concentrations above this inhibited hydrogenase activities, resulting in both lower hydrogen production and H<sub>2</sub>/CO<sub>2</sub> ratios. In addition, the results show that adding an appropriate amount of TEs not only enhanced biohydrogen development but also increased the ratio of H<sub>2</sub>/CO<sub>2</sub> up to 1. In Alshiyab et al.'s study, they reported that metal ions, such as Fe<sup>2+</sup>/Fe<sup>3+</sup> and Ni<sup>2+</sup>, facilitated an increase in hydrogen production during dark fermentation [15].

### 3.2. Effect of H<sub>2</sub>/CO<sub>2</sub> Ratio on Direct CO<sub>2</sub> Hydrogenation upon Adding Extra H<sub>2</sub> in Methanol Synthesis

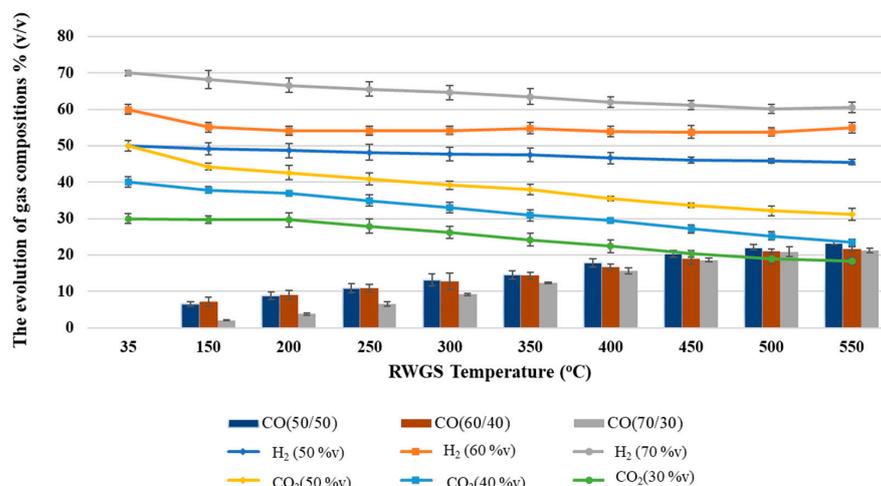
This biohydrogen experiment obtained a gas composition with a maximum H<sub>2</sub>/CO<sub>2</sub> ratio of approximately 1 (50/50% (v/v) H<sub>2</sub>/CO<sub>2</sub>). Following Equation (1), direct methanol synthesis normally requires a mole ratio for H<sub>2</sub>/CO<sub>2</sub> of approximately 3. Extra hydrogen was added to the system. After that, the effects of three different H<sub>2</sub>/CO<sub>2</sub> ratios, 50/50, 60/40, and 70/30% (v/v), were studied. Direct CO<sub>2</sub> hydrogenation was carried out at temperatures of 170, 200, and 230 °C with the TISTR optimum conditions (the pressure was fixed at 40 barg with under 5 kg of CuZnO/Al<sub>2</sub>O<sub>3</sub> at a total gas feed flow rate of 1 g/min (60 g/h)). As can be seen in Figure 6, the results showed that increasing the H<sub>2</sub>/CO<sub>2</sub> ratio resulted in an increase in the methanol production rate at every temperature applied: at 170 °C, the methanol production rates were 9.91, 12.01, and 13.15 g/h; at 200 °C, the production rates were 16.24, 17.00, and 17.81 g/h; and at 230 °C, the production rates were 10.91, 13.01, and 14.15 g/h. The optimum temperature was 200 °C, resulting in the maximum methanol amount. However, there is no evidence that a difference in the purity of the methanol product, which ranged from 61 to 63%, was related to CO<sub>2</sub> hydrogenation, as was also reported by Sarp S. in 2021 [16]. The methanol percentage obtained via the experiment showed that direct CO<sub>2</sub> hydrogenation followed Equation (3). The methanol percentage was over 50% because, during CO<sub>2</sub> hydrogenation, a side reaction involving the transformation of CO<sub>2</sub> into CO via RWGS appeared in parallel, as shown in Equation (4), which is related to the findings discussed in [17]. The gas mixture containing an amount of CO in the reaction resulted in some CO hydrogenation, which had a positive effect on the methanol yield of over 50%.



**Figure 6.** Direct methanol synthesis via CO<sub>2</sub> hydrogenation with varying H<sub>2</sub>/CO<sub>2</sub> ratios at a feed flow rate of 1 g/min. The bars represent methanol production (g/h), and the curves represent methanol purity in % by weight.

### 3.3. Effect of $H_2/CO_2$ Ratio on CO Generation in RWGS with Varying Temperatures

Direct methanol synthesis via  $CO_2$  hydrogenation gave a low methanol production rate, and the product was contaminated with a large amount of water, as shown in Figure 6. Therefore, indirect methanol synthesis via the transformation of  $CO_2$  into CO followed by CO hydrogenation may be a method for increasing methanol purity. The desired method was to apply the RWGS reaction (Equation (3)) to transform  $CO_2$  into CO before feeding it into the methanol synthesis process following Equation (2) for CO hydrogenation. This was expected to produce a higher methanol production rate than direct methanol synthesis. Therefore, the optimum ratio of  $H_2/CO_2$  would be the best for CO conversion via the RWGS. As in the previous section, the biohydrogen yielded a  $H_2/CO_2$  ratio of approximately 1. Therefore, the relationship between the  $H_2/CO_2$  feed ratio and the mixed gas product composed of  $H_2$ ,  $CO_2$ , and CO generated via the RWGS was studied. The results in the previous section demonstrated that adding  $H_2$  to the biohydrogen increased the normal  $H_2/CO_2$  % v/v or (mole ratio) of 50/50 (1/1) to 60/40 (1.49/1) and 70/30 (2.33/1). Three  $H_2/CO_2$  ratios for the RWGS with Cu/ZnO/ $Al_2O_3$  at temperatures ranging from 150 to 550 °C were studied. The results in Figure 7 show that the change in the % by vol. of  $H_2$  and  $CO_2$  (raw material gases) for all ratios decreased with an increase in the temperature from 150 to 500 °C and then  $CO_2$  and  $H_2$  slowly declined when a temperature between 500 and 550 °C was applied. The generation of CO increased from 150 to 500 °C and then slightly stabilized from 500 to 550 °C. This phenomenon follows Le Châtelier's principle as the reaction was endothermic; it was thermodynamically favored at higher temperatures until the CO and  $CO_2$  contents were balanced in equilibrium in the RWGS and WGS following the reverse reactions in Equations (3) and (4). In addition, increasing the  $H_2/CO_2$  ratio increased  $CO_2$  conversion and favored the RWGS reaction, as discussed by Chinchén [18]. The results showed that the RWGS equilibrium in Equation (3) dominated over the WGS in Equation (4), showing a % by vol. (mol) CO generation of approximately 21.20, 21.71, and 23.31 at 550 °C. Under all conditions, CO generation increased according to the increasing temperature, but the final amounts of CO conversion differed in terms of minimum numbers. This result can be explained by the moles of CO and  $CO_2$  being balanced in the RWGS and WGS conditions relating to Equations (3) and (4) [19–22]. In addition, the Cu/ZnO/ $Al_2O_3$  catalyst had a maximum temperature of approximately 550 °C, which followed the specification of the catalyst company. Therefore, the optimum temperature for  $CO_2/H_2$  in the RWGS was 500 °C, which was used in the RWGS reaction for safety reasons and generated the maximum CO and minimum  $CO_2$  contents.



**Figure 7.** Changes in gas compositions with varying  $H_2/CO_2$  ratios, and CO generation when applying different RWGS temperatures at a feed flow rate of 5 g/min.

### 3.4. The Comparison of H<sub>2</sub>/CO<sub>2</sub> Ratios for Methanol Synthesis via Two Pathways: (1) MS and MS and (2) RWGS and MS

Pathway 1 (DMS + DMS) was conducted as follows: two-step direct methanol synthesis was set up with two methanol synthesis reactors with a feed flow rate of 5 g/min, temperature of 200 °C, and pressure of 40 barg, as shown in Tables 2–4. The H<sub>2</sub>/CO<sub>2</sub> feed in unit % *v/v* (mol ratios) of 50/50 (1.00), 60/40 (1.50), and 70/30 (2.33) added to the first MS reactor resulted in methanol production rates of 0.43, 0.49, and 0.49 g/min. The feed contained only CO<sub>2</sub> and H<sub>2</sub> and then the reactions were followed by direct CO<sub>2</sub> hydrogenation via Equation (1), which produced a mixture of methanol and water around 61.43% (wt), 62.03% (wt), and 63.64% (wt), respectively. The off gas that came out of the first reactor contained mixed H<sub>2</sub>/CO<sub>2</sub>/CO % *v/v/v* (mol/min) of 44.17/45.45/10.38 (0.085/0.083/0.018), 53.52/36.80/9.67 (0.120/0.078/0.020), and 64.93/24.71/10.36 (0.195/0.070/0.028), respectively. There was clear evidence that an increase in the H<sub>2</sub>/CO<sub>2</sub> feed increased the % (wt) methanol purity and methanol production rate but generated almost no difference in CO generation, which was obtained from the side reaction following Equation (3). The mixed gas that was released from the first MS reactor turned into the feed in the second MS reactor in series. The results showed that the series of continual H<sub>2</sub>/CO<sub>2</sub> feed ratios of 50/50, 60/40, and 70/30 (%*v*) generated a percentage of CO in the mixed gas and resulted in higher mole ratios for H<sub>2</sub>/CO (4.70, 6.11, and 6.92) than for H<sub>2</sub>/CO<sub>2</sub> (1.03, 1.54, and 2.78), which supported the methanol synthesis via CO hydrogenation following Equation (2). As a result, the methanol concentration in the second step showed a higher yield compared with that in the first step, in which the methanol purity was 93.29% (wt), 94.16% (wt), and 80.39% (wt) and the methanol production rates were 0.50, 0.55, and 0.60 g/min. The mixed H<sub>2</sub>/CO<sub>2</sub>/CO % *v/v/v* (mol/min) values derived from the second reactor were 35.59/62.43/1.98 (0.050/0.082/0.003), 49.02/49.35/1.63 (0.080/0.077/0.003), and 63.94/31.64/4.41 (0.140/0.065/0.009), respectively. There was evidence that the mixed feed gas contained CO, which affected the selectivity of CO hydrogenation (Equation (2)) or CO<sub>2</sub> hydrogenation (Equation (1)). The first effect was that a lower percentage of CO<sub>2</sub> in the feed gas increased both the methanol production rates and the methanol purity (%), and the second effect was that a higher H<sub>2</sub>/CO ratio in the feed gas composition resulted in the reaction of Equation (2) competing with that of Equation (1). However, whilst the H<sub>2</sub>/CO<sub>2</sub> ratio was close to 3, the H<sub>2</sub>/CO ratio was over 2 following stoichiometry, and the methanol synthesis favored the reaction in Equation (1) over that in Equation (2), as shown in the 70/30% (*v/v*) H<sub>2</sub>/CO<sub>2</sub> feed case in the second reactor.

**Table 2.** Pathway 1: combining 1st MS and 2nd MS at a constant feed flow rate of 5 g/min and H<sub>2</sub>/CO<sub>2</sub> ratio of 50/50 (% *v/v*).

MS1_MS2	IN1	Out1	Out2	IN1	Out1	Out2	Total
	%v (mol/min)	%v (mol/min)	%v (mol/min)	g/min	g/min	g/min	g/min (mol/min)
H <sub>2</sub>	50 (0.11)	44.17 (0.085)	35.59 (0.050)	0.23	0.17	0.1	0
CO <sub>2</sub>	50 (0.11)	45.45 (0.083)	62.43 (0.082)	4.77	3.63	3.59	0
CO	0	10.38 (0.018)	1.98 (0.003)	0	0.51	0.07	0
Total gas	100 (0.22)	100 (0.186)	100 (0.134)	5	4.3	3.77	0
CH <sub>3</sub> OH	0	61.7 (0.013)	93.29 (0.016)	0	0.43	0.5	0.93 (0.029)
H <sub>2</sub> O	0	38.3 (0.015)	6.71 (0.002)	0	0.27	0.04	0.31 (0.017)
Total liquid	0	100 (0.028)	100 (0.018)	0	0.7	0.54	1.24 (0.046)
CO <sub>2</sub> conversion (g/min)							1.18
CO <sub>2</sub> consumption (%)							24.71
CH <sub>3</sub> OH concentration (%)					61.43	92.59	78.69
H <sub>2</sub> /CO <sub>2</sub> (mol/mol)	1	1.03					
H <sub>2</sub> /CO (mol/mol)		4.7					

**Table 3.** Pathway 1: combining 1st MS and 2nd MS at a constant feed flow rate of 5 g/min and H<sub>2</sub>/CO<sub>2</sub> ratio of 60/40 (% v/v).

MS1_MS2	IN1	Out1	Out2	IN1	Out1	Out2	Total
	%v (mol/min)	%v (mol/min)	%v (mol/min)	g/min	g/min	g/min	g/min (mol/min)
H <sub>2</sub>	60 (0.170)	53.52 (0.120)	49.02 (0.080)	0.34	0.24	0.16	0
CO <sub>2</sub>	40 (0.106)	36.8 (0.078)	49.35 (0.077)	4.66	3.42	3.39	0
CO	0	9.67 (0.020)	1.63 (0.003)	0	0.55	0.07	0
Total gas	100 (0.276)	100 (0.217)	100 (0.160)	5	4.21	3.63	0
CH <sub>3</sub> OH	0	62.2 (0.015)	94.16 (0.017)	0	0.49	0.55	1.04 (0.033)
H <sub>2</sub> O	0	37.8 (0.017)	5.84 (0.002)	0	0.3	0.03	0.33 (0.018)
Total liquid	0	100 (0.032)	100 (0.019)	0	0.79	0.58	1.37 (0.051)
CO <sub>2</sub> conversion (g/min)							1.27
CO <sub>2</sub> consumption (%)							27.32
CH <sub>3</sub> OH concentration (%)					62.03	94.83	75.91
H <sub>2</sub> /CO <sub>2</sub> (mol/mol)	1.5	1.54					
H <sub>2</sub> /CO (mol/mol)		6.11					

**Table 4.** Pathway 1: combining 1st MS and 2nd MS at a constant feed flow rate of 5 g/min and H<sub>2</sub>/CO<sub>2</sub> ratio of 70/30 (% v/v).

MS1_MS2	IN1	Out1	Out2	IN1	Out1	Out2	Total
	%v (mol/min)	%v (mol/min)	%v (mol/min)	g/min	g/min	g/min	g/min (mol/min)
H <sub>2</sub>	70 (0.250)	64.93 (0.195)	63.94 (0.140)	0.5	0.39	0.28	0
CO <sub>2</sub>	30 (0.102)	24.71 (0.070)	31.64 (0.065)	4.5	3.06	2.88	0
CO	0	10.36 (0.028)	4.41 (0.009)	0	0.78	0.25	0
Total gas	100 (0.352)	100 (0.292)	100 (0.214)	5	4.23	3.48	0
CH <sub>3</sub> OH	0	63.3 (0.015)	80.39 (0.019)	0	0.49	0.6	1.09 (0.034)
H <sub>2</sub> O	0	36.7 (0.016)	19.61 (0.008)	0	0.28	0.15	0.43 (0.024)
Total liquid	0	100 (0.031)	100 (0.027)	0	0.77	0.75	1.52 (0.058)
CO <sub>2</sub> conversion (g/min)							1.62
CO <sub>2</sub> consumption (%)							36.00
CH <sub>3</sub> OH concentration (%)					63.64	80.00	71.71
H <sub>2</sub> /CO <sub>2</sub> (mol/mol)	2.33	2.78					
H <sub>2</sub> /CO (mol/mol)		6.92					

Pathway 2 (IMS + DMS) was conducted as follows: the RWGS followed by methanol synthesis was set up. The first reaction with the RWGS reactor was operated at a feed flow rate of 5 g/min, a temperature of 500 °C, and atm pressure with H<sub>2</sub>/CO<sub>2</sub> feed ratios of 50/50 (1.00), 60/40 (1.50), and 70/30 (2.33). Then, it was connected with the second methanol synthesis reactor in series at 200 °C and 40 barg, and the results are shown in Tables 5–7. The result was clear: feeding a higher ratio of H<sub>2</sub>/CO<sub>2</sub> into the RWGS resulted in higher conversion following Equation (3), which resulted in a methanol concentration of 0%; water yields of 0.82, 1.79, and 2.54 g/min; and mixed H<sub>2</sub>/CO<sub>2</sub>/CO gas containing % (v/v/v) or (mol/min) 37.08/39.26/23.66 (0.065/0.067/0.039), 51.23/26.73/22.05 (0.095/0.046/0.036), and 62.68/17.70/19.62 (0.115/0.030/0.032), respectively. The RWGS converted CO<sub>2</sub> into CO following Equation (3), equating with the WGS following Equation (4), which resulted in the balancing of the ratio of CO<sub>2</sub> to CO. The equilibrium of RWGS and WGS resulted in the % CO (mol) generation being slightly reduced to 23.66 (0.039), 22.05 (0.036), and 19.62 (0.032), whereas it boosted the H<sub>2</sub>/CO ratios to 1.73, 2.56, and 3.53, respectively, which supported methanol synthesis via CO hydrogenation following Equation (2). The mixed gas that was released from the first RWGS reactor was collected in the LPT tank and the pressure was increased using the CP and then fed into the second MS reactor in series. The methanol concentration in the second step showed higher purity percentages of 95.81% (wt), 97.98% (wt), and 92.93% (wt) and methanol yields of 0.69, 1.01, and

1.05 g/min. The mixed H<sub>2</sub>/CO<sub>2</sub>/CO gas derived from the second reactor contained % v/v/v or (mol/min) 18.24/64.12/17.64 (0.020/0.067/0.018), 32.01/61.15/6.84 (0.025/0.045/0.005), and 57.54/40.10/2.36 (0.045/0.029/0.002), respectively. The results are the same as those for pathway 1, wherein the mixed feed gas containing CO then influenced the selectivity of CO hydrogenation (Equation (2)) or CO<sub>2</sub> hydrogenation (Equation (1)). The main effect was that a lower percentage of CO<sub>2</sub> in the feed gas increased both the methanol yield and the methanol purity %, and a higher H<sub>2</sub>/CO in the feed gas composition promoted the dominance of Equation (2) over Equation (1). However, the H<sub>2</sub>/CO<sub>2</sub> mole ratio was close to or over 3, and the reaction preferred CO<sub>2</sub> hydrogenation following Equation (1), resulting in a reduction in the methanol purity, as shown by the H<sub>2</sub>/CO<sub>2</sub> ratio for the 70/30 feed case in the second reactor.

**Table 5.** Pathway 2: combining 1st RWGS + 2nd MS at a constant feed flow rate of 5 g/min and H<sub>2</sub>/CO<sub>2</sub> ratio of 50/50 (% v/v).

RWGS1_MS2	IN1	Out1	Out2	IN1	Out1	Out2	Total
	%v (mol/min)	%v (mol/min)	%v (mol/min)	g/min	g/min	g/min	g/min (mol/min)
H <sub>2</sub>	50 (0.11)	37.08 (0.065)	18.24 (0.020)	0.23	0.13	0.04	0
CO <sub>2</sub>	50 (0.11)	39.26 (0.067)	64.12 (0.067)	4.77	2.96	2.93	0
CO	0	23.66 (0.039)	17.64 (0.018)	0	1.09	0.49	0
Total gas	100 (0.22)	100 (0.171)	100 (0.104)	5	4.18	3.46	0
CH <sub>3</sub> OH	0	0	95.81 (0.022)	0	0	0.69	0.69 (0.022)
H <sub>2</sub> O	0	100 (0.046)	4.19 (0.002)	0	0.82	0.03	0.85 (0.047)
Total liquid	0	100 (0.046)	100 (0.024)	0	0.82	0.72	1.54 (0.069)
CO <sub>2</sub> conversion (g/min)							1.84
CO <sub>2</sub> consumption (%)							38.61
CH <sub>3</sub> OH concentration (%)					0	95.81	95.81
H <sub>2</sub> /CO <sub>2</sub> (mol/mol)	1	1					
H <sub>2</sub> /CO (mol/mol)		1.73					

**Table 6.** Pathway 2: combining 1st RWGS + 2nd MS at a constant feed flow rate of 5 g/min and H<sub>2</sub>/CO<sub>2</sub> ratio of 60/40 (% v/v).

RWGS1_MS2	IN1	Out1	Out2	IN1	Out1	Out2	Total
	%v (mol/min)	%v (mol/min)	%v (mol/min)	g/min	g/min	g/min	g/min (mol/min)
H <sub>2</sub>	60 (0.170)	51.23 (0.095)	32.01 (0.025)	0.34	0.19	0.05	0
CO <sub>2</sub>	40 (0.106)	26.73 (0.046)	61.15 (0.045)	4.66	2.01	1.99	0
CO	0	22.05 (0.036)	6.84 (0.005)	0	1.01	0.14	0
Total gas	100 (0.276)	100 (0.177)	100 (0.075)	5	3.21	2.18	0
CH <sub>3</sub> OH	0	0	97.98 (0.032)	0	0	1.01	1.01 (0.032)
H <sub>2</sub> O	0	100 (0.099)	2.02 (0.001)	0	1.79	0.02	1.81 (0.001)
Total liquid	0	100 (0.099)	100 (0.033)	0	1.79	1.03	1.54 (0.069)
CO <sub>2</sub> conversion (g/min)							2.67
CO <sub>2</sub> consumption (%)							57.25
CH <sub>3</sub> OH concentration (%)					0	97.98	97.98
H <sub>2</sub> /CO <sub>2</sub> (mol/mol)	1.49	2.03					
H <sub>2</sub> /CO (mol/mol)		2.56					

**Table 7.** Pathway 2: combining 1st RWGS + 2nd MS at a constant feed flow rate of 5 g/min and H<sub>2</sub>/CO<sub>2</sub> ratio of 70/30 (% v/v).

RWGS1_MS2	IN1	Out1	Out2	IN1	Out1	Out2	Total
	%v (mol/min)	%v (mol/min)	%v (mol/min)	g/min	g/min	g/min	g/min (mol/min)
H <sub>2</sub>	70 (0.250)	62.68 (0.115)	57.54 (0.045)	0.5	0.23	0.09	0
CO <sub>2</sub>	30 (0.102)	17.7 (0.030)	40.1 (0.029)	4.5	1.33	1.26	0
CO	0	19.62 (0.032)	2.36 (0.002)	0	0.9	0.05	0
Total gas	100 (0.352)	100 (0.177)	100 (0.075)	5	2.46	1.33	0
CH <sub>3</sub> OH	0	0	92.93 (0.033)	0	0	1.05	1.05 (0.033)
H <sub>2</sub> O	0	100 (0.141)	7.07 (0.004)	0	2.54	0.08	2.62 (0.146)
Total liquid	0	100 (0.141)	100 (0.037)	0	2.54	1.13	3.67 (0.178)
CO <sub>2</sub> conversion (g/min)							3.24
CO <sub>2</sub> consumption (%)							72.02
CH <sub>3</sub> OH concentration (%)					0	92.93	92.93
H <sub>2</sub> /CO <sub>2</sub> (mol/mol)	2.33	3.74					
H <sub>2</sub> /CO (mol/mol)		3.53					

#### 4. Discussion

A comparison of the two-step methanol synthesis between pathway 1, DMS (MS + MS), and pathway 2, IMS (RWGS + MS), showed that pathway 2 resulted in lower methanol production rates (g/h) of 0.69, 1.01, and 1.05 than the 0.93, 1.04, and 1.09 obtained via pathway 1, but it resulted in higher average methanol purities % (wt) of 95.81, 97.98, and 92.93 than the purities obtained via pathway 1 (78.69, 79.10, and 72.71). It is apparent that the IMS pathway (adding RWGS before MS) for biohydrogen (H<sub>2</sub> and CO<sub>2</sub>) could improve the purity of the methanol more effectively than the DMS pathway because CO<sub>2</sub> was transformed into CO by the RWGS reaction following Equation (3) and limited by the WGS reaction, as in Equation (4). The evolution of CO<sub>2</sub> into CO depended on the conditions (CO/CO<sub>2</sub> mole ratio, temperature, and pressure). The CO<sub>2</sub> was transformed by reacting it with H<sub>2</sub>, and CO was generated, obtaining the optimum H<sub>2</sub>/CO ratio of around 2 as the stoichiometry followed Equation (2). These were the optimum conditions for generating high-purity biomethanol (97.98%), as obtained in the experiment with H<sub>2</sub>/CO<sub>2</sub> at 60/40% (v/v). Otherwise, the mole ratio of H<sub>2</sub> to CO over 2 was partly caused by the higher ratio of H<sub>2</sub>/CO<sub>2</sub> in the raw gas feed, at 70/30% (v/v), or 2.33/1 (mol/mol); in this case, there was a higher ratio, over 3, for both H<sub>2</sub>/CO<sub>2</sub> (3.74) and H<sub>2</sub>/CO (3.53). As a result, CO<sub>2</sub> hydrogenation (Equation (1)) competed with CO hydrogenation (Equation (2)), and water was generated and mixed with methanol, resulting in the methanol purity being reduced to 92.93%. Therefore, the IMS would be expected to produce a higher methanol yield than DMS.

Although the IMS was beneficial in terms of both methanol purity and CO<sub>2</sub> consumption, the RWGS step in IMS was an endothermic reaction that required a higher temperature (500 °C) than that required for the MS step (200 °C); hence, it consumed more energy in methanol production. Last but not least, the overall energy consumption should be studied in greater depth for overall processes, including methanol synthesis and methanol refinery.

#### 5. Conclusions

The focus of this work was on the added value of turning molasses into biohydrogen over biogas for biomethanol synthesis. It was clear that CO<sub>2</sub> utilization achieved by adding a small amount of H<sub>2</sub> for methanol synthesis would create an opportunity to use molasses to produce biomethanol. Our results reveal that RWGS performed before DMS supported CO hydrogenation, and the transformation of biohydrogen into biomethanol (1) provided higher methanol concentrations, approaching the concentration of commercial methanol (99.9%), (2) necessitated a small refinery, and (3) increased CO<sub>2</sub> consumption, which creates an opportunity to apply this knowledge for the management of CO<sub>2</sub>, called CO<sub>2</sub> utilization.

Taken together, this novel frontier of the implementation of the RWGS process will better support commercial methanol synthesis.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## Nomenclature

%	Percent
% ( <i>v/v</i> )	Percent by volume
% (wt).	Percent by weight
°C	Celsius
1st MS	First methanol synthesis
2nd MS	Second methanol synthesis
Ave.	Average
barg	Bar (guage pressures)
cm	Centimeter
CS1	Cool separator 1
CS2	Cool separator 2
DME	Dimethyl ether
DMS	Direct methanol synthesis
E.A.	<i>Enterobacter aerogenes</i>
g	Gram
g/L	Grams per liter
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
HPT	High pressure tank
h	Hour
IMS	Indirect methanol synthesis
kg	Kilogram
kJ/mol	Kilojoules per mole
LPT	Low-pressure tank
MC	Molasses concentration
MFBH	Mass flow of biohydrogen
MFC	Mass flow of carbon dioxide
MFH	Mass flow of hydrogen
MFN	Mass flow of nitrogen
MFSG	Mass flow of syngas
min	Minute
Mol.	Molasses
MS	Methanol synthesis
MTBE	Methyl tertiary butyl ether
MTO	Methanol to olefin

MTP	Methanol to paraffin
RWGS	Reverse water–gas shift
RX1	Reactor 1
RX2	Reactor 2
TAME	Tert-amyl methyl ether
TE	Trace elements
Try.	Tryptone
TSBS	Two-step biomethanol synthesis
WGS	Water–gas shift

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