



# Exploring the Thermodynamic Limits of Enhanced H<sub>2</sub> Recovery With Inherent Carbon Removal From Low Value Aqueous Biomass Oxygenate Precursors

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Rational integration of chemical pathways at the molecular scale to direct thermodynamically favorable enhanced H<sub>2</sub> production with inherent carbon removal from low-value substrates can be guided by exploring the thermodynamic limits of feasibility. The substrates of interest are biomass oxygenates that are water-soluble and uneconomical for separation from water. In this study, we investigate the thermodynamic feasibility of recovering H<sub>2</sub> with inherent carbon removal from biomass oxygenates such as ethanol, methanol, glycerol, ethylene glycol, acetone, and acetic acid. The influence of biomass oxygenate-to-water ratios, reaction temperature of 150°C–325°C, and CaO or Ca(OH)<sub>2</sub> as the alkalinity source on the yields of H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and Ca-carbonate are investigated. By maintaining the fluids in the aqueous phase under pressure, energy needs associated with vaporization are circumvented. The hypothesis that enhanced alkalinity favors the preferential formation of CO (precursor for CO<sub>2</sub> formation) over CH<sub>4</sub> and aids the formation of calcium carbonate is investigated. The findings from these studies inform the feasibility, design of experiments, and the tuning of reaction conditions for enhanced H<sub>2</sub> recovery with inherent carbon removal from biomass oxygenate sources.

**Keywords:** hydrogen, carbon removal, biomass oxygenates, calcium carbonate, thermodynamics

## INTRODUCTION

Decarbonizing energy carriers such as H<sub>2</sub> while upcycling abundant low value resources is crucial for a sustainable energy, environmental, and climate future. This approach addresses our societal mission of lifting millions of people out of energy poverty globally (WHO, 2009) while limiting detrimental environmental impacts including the rise of global temperatures (Masson-Delmotte

**Abbreviations:**  $\Delta H_{298}^0$ , standard heat of reaction at 298 K G total Gibbs free energy of the system;  $G_i^0$ , Gibbs free energy of species *i* at its standard state; *T*, temperature; *R*, universal gas constant;  $z_i P$ , partial pressure of species *i* in the gas phase;  $n_i$ , number of moles of species *i*;  $\alpha_{ik}$ , number of atoms of *k*th component present in each molecules of species *i*;  $b_k$ , total number of atomic masses of *k*th component in the system;  $BO_{in}$ , amount of biomass oxygenates fed into the system;  $BO_{out}$ , amount of biomass oxygenates unconverted; SR, H<sub>2</sub>/BO stoichiometric ratio.

**TABLE 1** | Concentration of methanol, ethanol, glycerol, ethylene glycol, acetone, and acetic acid in waste streams.

Biomass oxygenate of interest	Waste source	Concentration in mg/L	References
Methanol	Wastewater algae	0.022–0.5	Mincer and Aicher (2016)
	Industrial wastewater	1,000	Novak et al. (1985)
	Municipal wastewater	0.145–0.203	Kim et al. (2018)
Ethanol	Wastewater algae	30–530	Ellis et al. (2012)
	Industrial wastewater	18,500–49,400	Abanoz et al. (2012)
	Municipal wastewater	235–245	Ajao et al. (2019)
	Food waste	58,000	Uçkun Kiran and Liu (2015)
Glycerol	Municipal wastewater	84,850–89,890	Yan et al. (2012)
	Industrial wastewater (bio-diesel)	400–420	Ajao et al. (2019)
Ethylene Glycol	Industrial wastewater	75,680–202,312	Thompson and He (2006)
	Wastewater algae	30–1,050	Qi et al. (2020)
Acetone	Wastewater algae	450–1,430	Ellis et al. (2012)
Acetic acid	Municipal wastewater	1884–2,520	Badawi et al. (1992)
	Food waste	12,810–25,880	Li et al. (2015)

et al., 2018). Currently, more than 85% of H<sub>2</sub> is produced *via* steam methane reforming (SMR) and the water gas shift reaction (WGSR) as represented by the following reactions: CH<sub>4</sub> + H<sub>2</sub>O → CO + 3H<sub>2</sub> (SMR) and CO + H<sub>2</sub>O → CO<sub>2</sub> + H<sub>2</sub> (WGSR). Producing H<sub>2</sub> from renewable natural gas (e.g., biogas) and removing CO<sub>2</sub> is one approach to produce decarbonized fuels (Gadikota, 2020, 2021).

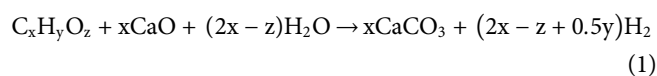
Conventional approaches to capture CO<sub>2</sub> using adsorption, (Sayari et al., 2011) absorption, (Rochelle, 2009), and membrane separations (Khalilpour et al., 2015) are being realized at the commercial scale. Once CO<sub>2</sub> is captured, it is compressed and stored in geologic formations (Benson and Surles, 2006). However, the availability of appropriate reservoirs for geologic storage of CO<sub>2</sub> is essential. In places that do not have access to appropriate geologic formations, alternative technologies are needed for storing CO<sub>2</sub> as inorganic carbonates. Further, energy carriers such as H<sub>2</sub> can be produced from distributed bio-based feedstocks with inherent carbon removal.

Significant advancements have been made in harnessing hydrogen from bio-based sources. Technologies to harness H<sub>2</sub> from gaseous and solid biomass-based feedstocks include steam reforming (SR) in which light hydrocarbons are reacted with steam to produce H<sub>2</sub> and CO<sub>2</sub>, usually in the presence of a catalyst (Ross, 1984; Ming et al., 2002), partial oxidation in which biomass is partial combusted with limited amount of O<sub>2</sub> to produce synthetic gas (a mixture of CO and H<sub>2</sub>) (Dissanayake et al., 1991; Hohn and Schmidt, 2001), and autothermal reforming (ATR) in which biomass is mixed with steam, and a limited amount of O<sub>2</sub> to produce synthetic gas and CO<sub>2</sub> (Dissanayake et al., 1991; Joensen and Rostrup-Nielsen, 2002; Deluga et al., 2004). Alkaline hydrothermal treatment (ATT) of wet biomass has been extensively reported to enhance H<sub>2</sub> generation from wet biomass with inherent CO<sub>2</sub> capture to produce inorganic carbonates (Stonor et al., 2017a; Zhang et al., 2020). However, few approaches have addressed strategies to harness H<sub>2</sub> from aqueous biomass oxygenate streams.

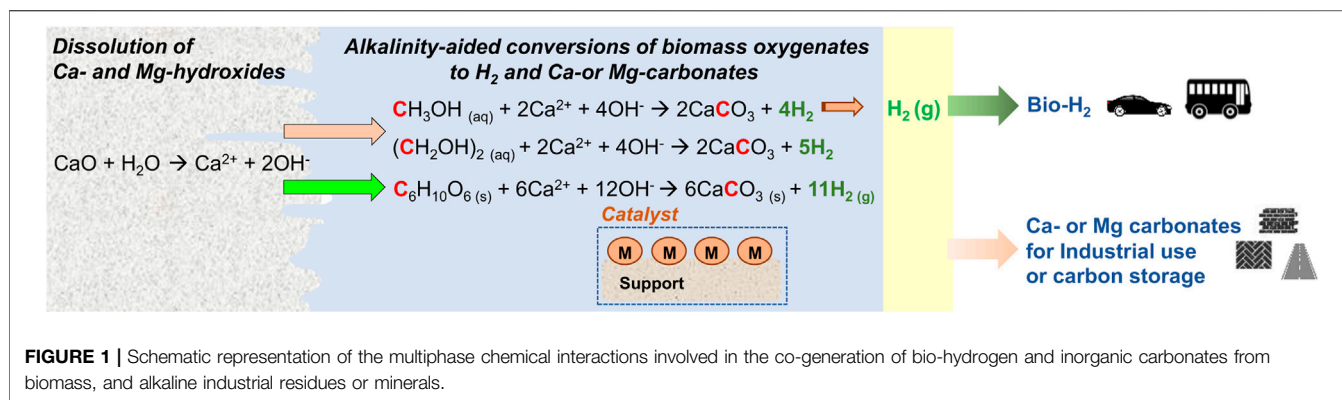
Biomass oxygenates soluble in water are important because they can be readily obtained from low value biomass feedstocks

such as food or municipal waste generated in urban or rural environments, algal sources, and industrial wastewater polluted streams as shown in **Table 1**. These feedstocks are also available in large quantities. For example, more than 40% of the food produced in the United States, and 44 million m<sup>3</sup>/day of wastewater generated in India, eventually returns to the environment as waste (Ranade and Bhandari, 2014; NRDC, 2021). Novel conversion pathways that can be easily adapted to accommodate a wide range of aqueous feedstocks are required, given the increasing scientific viability of producing simpler biomass oxygenates from waste streams, (Badawi et al., 1992; Thompson and He, 2006; Abanoz et al., 2012; Ellis et al., 2012; Yan et al., 2012; Li et al., 2015; Uçkun Kiran and Liu, 2015; Mincer and Aicher, 2016; Kim et al., 2018; Ajao et al., 2019; Qi et al., 2020; Arora et al., 2021) and from the chemical deconstruction of biomass (Brandt et al., 2013).

One such approach is aqueous phase reforming (APR) in which bio-derived aqueous feedstocks can be converted to H<sub>2</sub> in a pressurized environment. (Shabaker et al., 2003; Wen et al., 2008; Cortright et al., 2010). Compared to the other energy conversion approaches, APR occurs at 200–250°C which is significantly lower than temperatures >500°C for other biomass conversion approaches. The water gas shift reaction (WGSR) is integral to APR and catalysts are harnessed to direct the conversion of biomass oxygenates into H<sub>2</sub>. APR reactions are represented as follows: C<sub>n</sub>H<sub>2y</sub>O<sub>n</sub> + nH<sub>2</sub>O → nCO<sub>2</sub> + (y + n)H<sub>2</sub> (Davda et al., 2005). The approach of maintaining water in the aqueous phase as opposed to in the gas phase enables the scientific possibility of integrating with carbon mineralization reaction to remove CO<sub>2</sub> with H<sub>2</sub> recovery from biomass oxygenates (see **Figure 1**). The reaction representing H<sub>2</sub> recovery with inherent carbon removal is shown as follows:



The standard heats of reaction ( $\Delta H_{298}^0$ ) for methanol, ethanol, glycerol, ethylene glycol, acetone, and acetic acid are exothermic as shown in **Table 2**.



**TABLE 2 |** Standard heats of reaction (kJ/mol) for H<sub>2</sub> recovery from aqueous biomass oxygenates with inherent carbon removal: C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>(l) + xCaO(s) + (2x - z)H<sub>2</sub>O(l) → xCaCO<sub>3</sub>(s) + (2x - z + 0.5y)H<sub>2</sub>(g). Heat of formations for reacting and product species was obtained from (Williams, 1996).

Biomass oxygenate	Standard heats of reaction (kJ/mol)	Heat of reaction at 500 K (227°C) (kJ/mol)
Methanol	-47.7	-65.6
Ethanol	-10.4	-63.3
Glycerol	-191.1	-254.7
Ethylene glycol	-113.8	-153.0
Acetone	-40.7	-134.0
Acetic acid	-89.5	-128.1

Despite the simplicity of this stoichiometric representation, this reaction pathways are complex and involve several multiphase chemical interactions including: (i) cleavage of biomass oxygenate molecules, (ii) competitive formation of CO versus CH<sub>4</sub>, and (iii) conversion of CO to CO<sub>2</sub> followed by the subsequent dissolution of CO<sub>2</sub> to produce inorganic carbonates. These reactions are sensitive to temperature, pH, and solid and water compositions (in addition to catalyst compositions and uses). Further the anomalous solubility of calcium carbonate which decreases with increase in temperature and the dissolution behavior of the alkaline sources (e.g., Ca- or Mg-rich residues and minerals) in these multiphase chemical environments needs to be considered. The thermodynamic basis for these experimental investigations needs to be developed prior to demonstrating experimental feasibility. Therefore, the aim of this study is to develop the thermodynamic limits for enhanced H<sub>2</sub> recovery with inherent carbon removal from aqueous biomass oxygenates and alkaline sources such as calcium oxide (CaO). CaO is abundant in ash, slags, and kiln dusts recovered from industrial processes (Gadikota et al., 2015). The biomass oxygenates of interest are methanol (CH<sub>3</sub>OH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), glycerol [C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>], ethylene glycol [C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>], acetone (CH<sub>3</sub>COCH<sub>3</sub>), and acetic acid (CH<sub>3</sub>COOH), because these oxygenates have been frequently used as model compounds, during aqueous phase reforming at low temperatures (< 500°C) (Davda et al., 2005; Cortright et al., 2010; Coronado et al., 2016; NRDC, 2021). Also, these oxygenates are readily available in low value aqueous streams such as wastewater from biomass processing as shown in **Table 1**.

Prior studies focused on enhanced H<sub>2</sub> conversion from biomass feedstocks at high temperature and low pressure conditions in which steam is the dominant reacting phase as opposed to water. Temperatures in the range of 427°C–627°C and steam-to-biomass ratios greater than five resulted in highly selective H<sub>2</sub> production over CH<sub>4</sub> formation. However, this approach is accompanied by significant evolution of CO<sub>2</sub> and CO in the product stream (Cohce et al., 2010). H<sub>2</sub> with purity of 99.97% or higher is needed for fuel cell applications. Even low concentrations of CO to the order of 100 ppm can inhibit the use of fuel cells (Baschuk and Li, 2001; U.S. Department of Energy et al., 2016).

Thermodynamic analyses of methanol reforming found that temperatures of 246°C and steam-to-methanol ratio of 5.6 resulted in a maximized H<sub>2</sub> yield of 4.28% with methanation CH<sub>4</sub> and 99.7% without methanation reactions. Further, CO product formation at atmospheric pressure was minimized (Özcan and Akın, 2019). Coupling these reactions with CO<sub>2</sub> capture can ensure high purity H<sub>2</sub> yields for use in fuel cell applications. To investigate the influence of inherent CO<sub>2</sub> capture during H<sub>2</sub> recovery from biomass oxygenates, sorption-enhanced steam methane reforming was investigated. Equilibrium H<sub>2</sub> concentrations of over 97% were observed for reforming with water-to-oxygenate ratio of 6, 9, 4, and 12 for ethanol, glycerol, methanol, and n-butanol respectively, in the presence of CaO at 500°C, and at an elevated pressure of 5 bar (Lima Da Silva and Müller, 2011).

Furthermore, experimental studies building on similar conditions have reported better H<sub>2</sub> yields using catalysts that suppress CH<sub>4</sub> formation and favor more H<sub>2</sub> production. For example, H<sub>2</sub> yield of 63% was noted using 10 wt% aqueous glycerol in the presence of CaO and Pt-Ni catalyst at 230°C and initial N<sub>2</sub> pressure of 30 bar (He et al., 2015). Maintaining the fluid in the aqueous phase favors accelerated carbon mineralization *via* enhanced dissolution and carbonate formation. Extensive studies reported the use of appropriate catalysts for aqueous phase reforming (Davda et al., 2005; Luo et al., 2008; Menezes et al., 2011; De Vlioger et al., 2012; Roy et al., 2012). Catalysts that preferentially direct the formation of CO over CH<sub>4</sub> in aqueous phase reforming were reported. However, comprehensive analyses exploring the thermodynamic limits of enhanced H<sub>2</sub> recovery with CO<sub>2</sub> capture from biomass

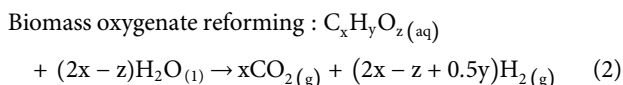
oxygenates and the corresponding physico-chemical parameters have not been reported in prior literature. This information is essential for developing the rational basis for enhanced H<sub>2</sub> recovery from biomass oxygenates with inherent carbon removal while maintaining the fluid in the aqueous phase.

In this study, the compositions of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> in the gas phase are determined as a function of temperature, water-to-oxygenate ratios, and CaO compositions for various biomass oxygenates such as ethanol, methanol, glycerol, ethylene glycol, acetic acid, and acetone. Specifically, the enhancement in H<sub>2</sub> yield due to inherent carbon removal via calcium carbonate formation is the focus of these investigations. These studies provide the basis for experimental studies for probing enhanced H<sub>2</sub> yield from biomass oxygenates with inherent carbonate formation.

## METHODS

### Reactions Involved in Enhanced H<sub>2</sub> Recovery With Inherent Carbon Removal From Aqueous Biomass Oxygenates

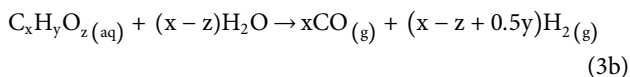
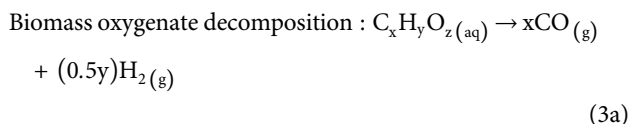
Several reactions and intermediate steps are involved in the recovery of H<sub>2</sub> from biomass oxygenates with the inherent removal of CO<sub>2</sub>. These reactions are incorporated into the models for exploring thermodynamic limits for enhanced H<sub>2</sub> recovery with carbon removal via mineralization. Reaction 2 represents the deconstruction of biomass oxygenates to produce CO<sub>2</sub> and H<sub>2</sub>. This reaction represents the overall pathway for biomass oxygenate refining without CO<sub>2</sub> capture.



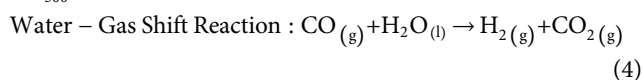
Standard heat of reaction ( $\Delta H_{500}^0$ ) = 108.6<sup>a</sup>, 285.2<sup>b</sup>, 268.1<sup>c</sup>, 195.5<sup>d</sup>, 388.7<sup>e</sup>, 220.3<sup>f</sup> kJ mol<sup>-1</sup>

a, b, c, d, e, f corresponds to methanol, ethanol, glycerol, ethylene glycol, acetone, and acetic acid, respectively.

Reaction 2 involves several intermediate steps as described below. The first step in this pathway is the preferential formation of CO through bio-oxygenate decomposition as shown in Eq. 3a for C:O molar ratio of 1:1, and hydrolysis as shown in Eq. 3b for C:O molar ratios greater than 1:1. The CO produced then undergoes an exothermic water gas shift reaction (WGSR) to produce H<sub>2</sub> and CO<sub>2</sub>.

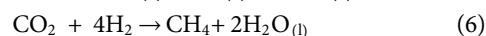
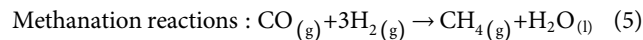


$$\Delta H_{500}^0 = 127.1^g, 322.2^b, 323.6^c, 232.5^h, 444.2^e, 257, 2^i \text{ kJmol}^{-1}$$



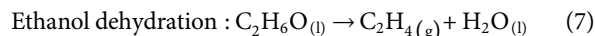
$$\Delta H_{500}^0 = -18.5 \text{ kJmol}^{-1}$$

Competing reactions that result in CH<sub>4</sub> formation as opposed to H<sub>2</sub> formation need to be incorporated (see reactions 5 and 6). Compared to WGS reactions, methanation reactions are more exothermic which make them favorable at low temperatures.

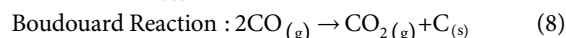


$\Delta H_{500}^0 = -235.6 \text{ kJmol}^{-1}$  and  $\Delta H_{500}^0 = -217.1 \text{ kJmol}^{-1}$  for Eqs 5, 6 respectively.

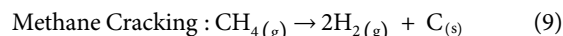
Furthermore, bio-derived oxygenates and their intermediate products can undergo dehydration, cracking, decomposition, and reduction to produce more undesired products such as CH<sub>4</sub>, CO, solid C, and C<sub>2</sub>H<sub>4</sub>, as shown by reactions 7–11 below.



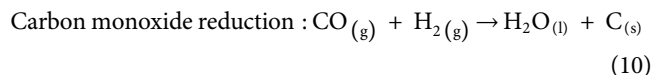
$$\Delta H_{500}^0 = 58.4 \text{ kJmol}^{-1}$$



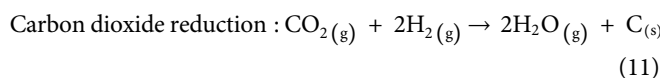
$$\Delta H_{500}^0 = -173.8 \text{ kJmol}^{-1}$$



$$\Delta H_{500}^0 = 80.3 \text{ kJmol}^{-1}$$

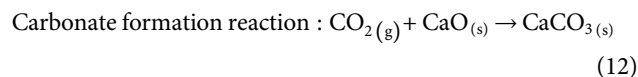


$$\Delta H_{500}^0 = -155.3 \text{ kJmol}^{-1}$$



$$\Delta H_{500}^0 = -136.8 \text{ kJmol}^{-1}$$

Bio-oxygenate reforming reactions can be endothermic. Therefore, coupling these with exothermic carbon mineralization reactions (Eq. 12) enhances the overall spontaneity of these reactions. The overall exothermicity resulting from the coupling of these reaction is shown in Eq. 1, and the heat of reactions at 500 K for methanol, ethanol, glycerol, ethylene glycol, acetone, and acetic acid is presented in Table 2.

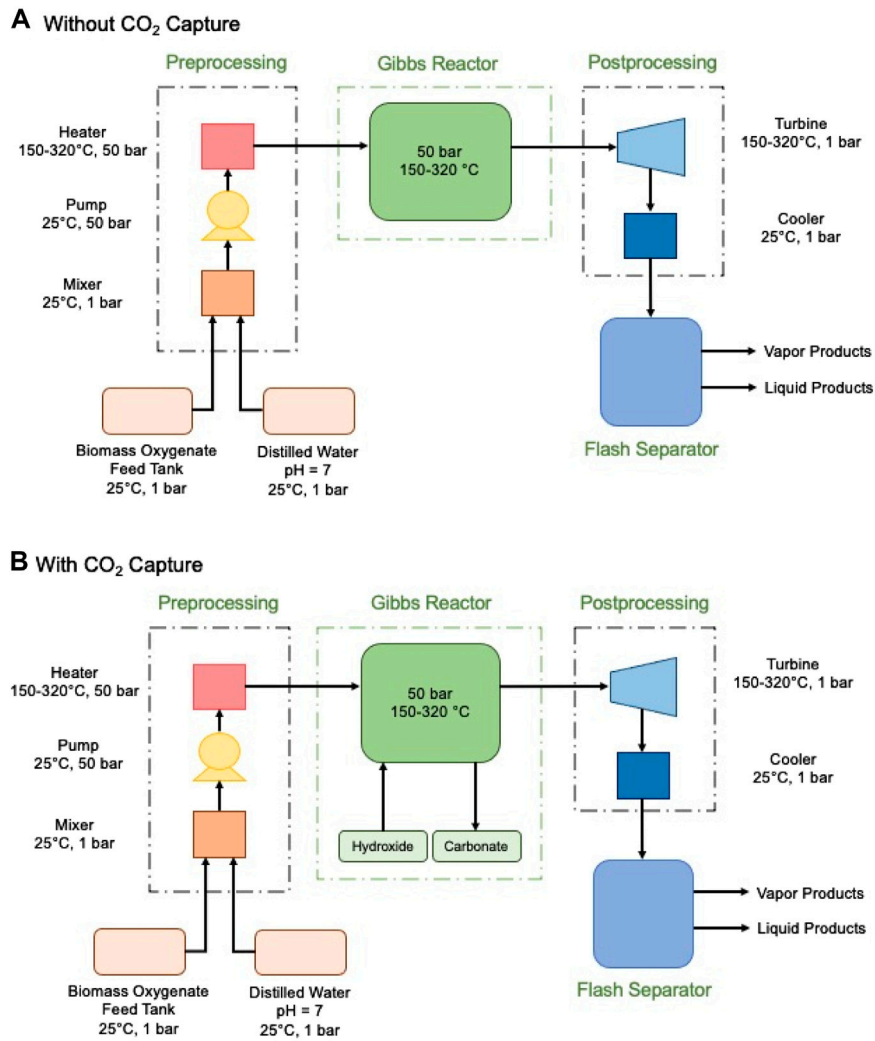


$$\Delta H_{500}^0 = -174.3 \text{ kJmol}^{-1}$$

### Thermodynamic Modelling and Simulation Methodology

The equilibrium compositions of various reacting processes are determined using the Gibbs energy minimization method. A more detailed description of this methodology was described by Lima *et al.* (Lima da Silva *et al.*, 2009; Lima Da Silva and Müller, 2011). The advantage of this approach is that it addresses systems with potential for simultaneous reactions. The objective function shown in Eq. 14 is minimized subject to the elemental balance constraint in Eq. 15,





**FIGURE 2 |** Process flow diagram of simulation environment **(A)** without *in-situ* CO<sub>2</sub> capture, **(B)** with *in-situ* CO<sub>2</sub> capture. The thermodynamic feasibility of enhancing H<sub>2</sub> recovery with inherent carbon removal using aqueous biomass oxygenate sources are based on the reactions taking place in the Gibbs reactor.

$$\frac{G}{RT} = \left\{ \sum_{i=1}^N n_i \left[ \frac{G_i^0}{RT} + \ln(z_i P) \right] \right\} + \frac{1}{RT} \sum_{j=1}^N n_j G_j^0 \quad (14)$$

$$\sum_{j=1}^N n_j \alpha_{jk} + \sum_{i=1}^N n_i \alpha_{ik} = b_k \quad K = 1 \dots M \quad (15)$$

Where  $G$ ,  $G_i^0$ ,  $T$ ,  $R$ ,  $z_i$ ,  $P$ ,  $n_j$ ,  $\alpha_{jk}$ , and  $b_k$  represents the total Gibbs free energy of the system, Gibbs free energy of species  $i$  at its standard state, temperature of the system, universal gas constant, mole fraction of species  $i$  in the gas phase, pressure of the system, number of atoms of  $k$ th component present in each molecules of species  $i$ , and the total number of atomic masses of  $k$ th component in the system, respectively.

Minimizing the objective function of the system indicates that a mixture of chemical species approaches an equilibrium state. These equilibrium calculations were performed and simulated using ASPEN® Plus V8.6 process simulation software. The Gibbs reactor (see **Figure 2A,B**) was modelled as an Isothermal

equilibrium reactor, which calculates the equilibrium composition of product species using the Gibbs energy minimization method at various operating conditions, keeping our reaction temperature constant, while accounting for the heat of reactions. The Peng-Robinson (Peng-Rob) equations of state were used to model the property parameter (Peng and Robinson, 1976). This property method has been widely used for processes containing oxygenates, water, and combustion gases (Fateen et al., 2013; Ali et al., 2014; Jimmy et al., 2017).

Prior to been fed into the reactor, biomass oxygenate, and water is mixed, pressurized, and heated using a mixer, pump, and heater, respectively. In cases where the effect of alkalinity was investigated, the alkaline source was fed directly into the reactor at its specified temperature and pressure. It was found that the temperature of the input feed stream does not affect the thermodynamic results, because fixing the reactor parameters produces the equilibrium effect determined by the set

temperature and pressure. However, the configuration was still used to ensure proper representation of the real batch reformer, as it would account for the energy required to heat the feedstock to the desired temperature and cool the products before analysis. Using this setup, H<sub>2</sub> evolution with varying biomass oxygenate-to-water ratios in the range of 5–95%, a low temperature range of 150–325°C, and varying alkaline sources, was studied at 50 bar. Prior studies have shown that methanation reactions can also be effectively suppressed using catalysts (Davda et al., 2005; Coronado et al., 2016). We also investigated the influence of 1) methanation and 2) suppressed methanation. Both cases were also investigated with and without CO<sub>2</sub> capture *via* carbon mineralization. This approach provides the optimal and sub-optimal scenarios that are dependent on the activity of the catalysts.

The equilibrium conversions of biomass oxygenates to products and associated product yields were defined as follows:

$$\begin{aligned} & \% \text{ Conversion of Biomass Oxygenates (BO)} \\ &= \frac{\text{BO}_{\text{in}} - \text{BO}_{\text{out}}}{\text{BO}_{\text{in}}} * 100 \end{aligned} \quad (17)$$

$$\begin{aligned} & \% \text{H}_2 \text{ yield} \\ &= \left[ \frac{\text{Moles of H}_2 \text{ produced}}{\text{Moles of biomass oxygenate fed} * \text{Stoichiometric Ratio (SR)}} \right] * 100 \end{aligned} \quad (18)$$

$$\begin{aligned} & \% \text{CO, CO}_2 \text{ and alkanes yield} = \frac{\text{Moles of C in compound produced}}{\text{Moles of C atoms in BO fed}} * 100 \end{aligned} \quad (19)$$

## RESULTS AND DISCUSSION

### Effect of Water-to-Biomass Oxygenate Ratio on H<sub>2</sub> Recovery With Carbon Removal

Water plays a synergistic role in enhanced H<sub>2</sub> recovery with inherent carbon removal from biomass oxygenates. Water facilitates the dissolution of calcium oxide to release calcium ions that can readily react with the evolved CO<sub>2</sub> to produce inorganic carbonates, as opposed to steam. The enhanced ion transport in gas-liquid-solid environments as opposed to in gas-solid environments favors accelerated formation of carbonates at lower temperatures as opposed to sorption-enhanced steam methane reforming that occurs at higher temperatures (Wang et al., 2008; Lindén et al., 2011). Further, the need for additional energy input in the form of latent heat of vaporization is avoided by maintaining water in the aqueous phase. To harness these advantages and resolve the compositions of the product stream, simulations were performed at 227°C, N<sub>2</sub> pressure of 50 bar, with and without stoichiometric amounts of CaO as defined by reaction 1 and 13. H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> yields with and without CaO are shown in **Figures 3–8** for methanol, ethanol, glycerol, ethylene glycol, acetone, and acetic acid, respectively.

In the absence of CaO for CO<sub>2</sub> capture, the yields of H<sub>2</sub> and CH<sub>4</sub> remain unaffected by an increase in the concentration of methanol and ethanol up to 40 wt% (See **Figures 3A,C, 4A,C**). Further increases in the concentrations of methanol and ethanol led to an increase in CH<sub>4</sub> yield and a simultaneous decrease in the production of hydrogen.

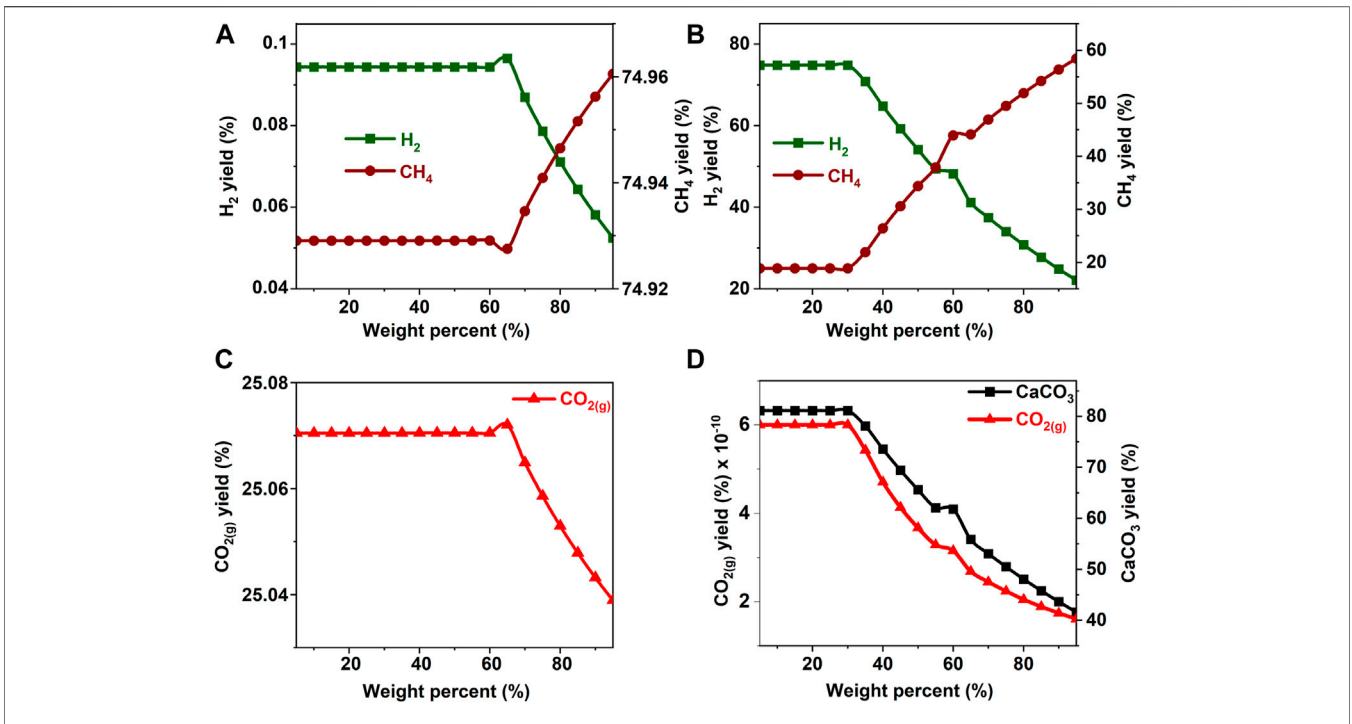
Decrease in H<sub>2</sub> yield is accompanied by a decrease in the production of gaseous CO<sub>2</sub> gas, which can be attributed to the limited amount of H<sub>2</sub>O available to undergo a water gas shift reaction as shown in **Eq. 4**. Limited water concentration cause a thermodynamic shift to favor CH<sub>4</sub> production *via* CO methanation reaction at equilibrium. When CaO was introduced to capture CO<sub>2</sub>, H<sub>2</sub> concentrations decreased after methanol and ethanol concentrations exceeded 20 wt% (See **Figures 3B,D, 4B,D**). This change is attributed to the use of water for the water gas shift reaction and the dissolution of CaO to produce calcium carbonate.

The hypothesis that CaO significantly enhances H<sub>2</sub> yields and suppresses CH<sub>4</sub> yields was shown to be true since H<sub>2</sub> yields exceeding 75% were achieved around 20 wt% for all the biomass oxygenates reported in this study (**Figures 3B–8B**). In the absence of CaO, less than 2% yield of H<sub>2</sub> was noted (**Figures 3A–8A**). However, methane yields either remained unchanged at low biomass oxygenate concentrations or increased in most cases except for acetone. At acetone concentrations of 80 wt% or higher, H<sub>2</sub> yields approached zero and methane yields decreased significantly. Also, the concentration of unreacted acetone in the product stream rapidly increased indicating low conversions of acetone (19–81%) at concentrations of 80wt% or higher, elsewhere the conversion was 100%. The observed anomaly could imply a different reaction mechanism caused by inadequate amounts of water leading to acetone decomposition to produce unstable radicals described as (CH<sub>3</sub>COCH<sub>3</sub> → 2CH<sub>3</sub><sup>\*</sup> + CO) (Spence and Wild, 1936; Smith and Hinshelwood, 1944). Further, the absence of H<sub>2</sub>O or H<sub>2</sub> for the CO produced during this reaction to undergo WGS reactions or methanation reaction as described in reactions 4) and 5) shifts the equilibrium back to acetone production at room temperature, leading to low conversions. With all the biomass oxygenates investigated, non-monotonic relationships between the concentrations of biomass oxygenates and the yields of H<sub>2</sub> and CH<sub>4</sub> were noted.

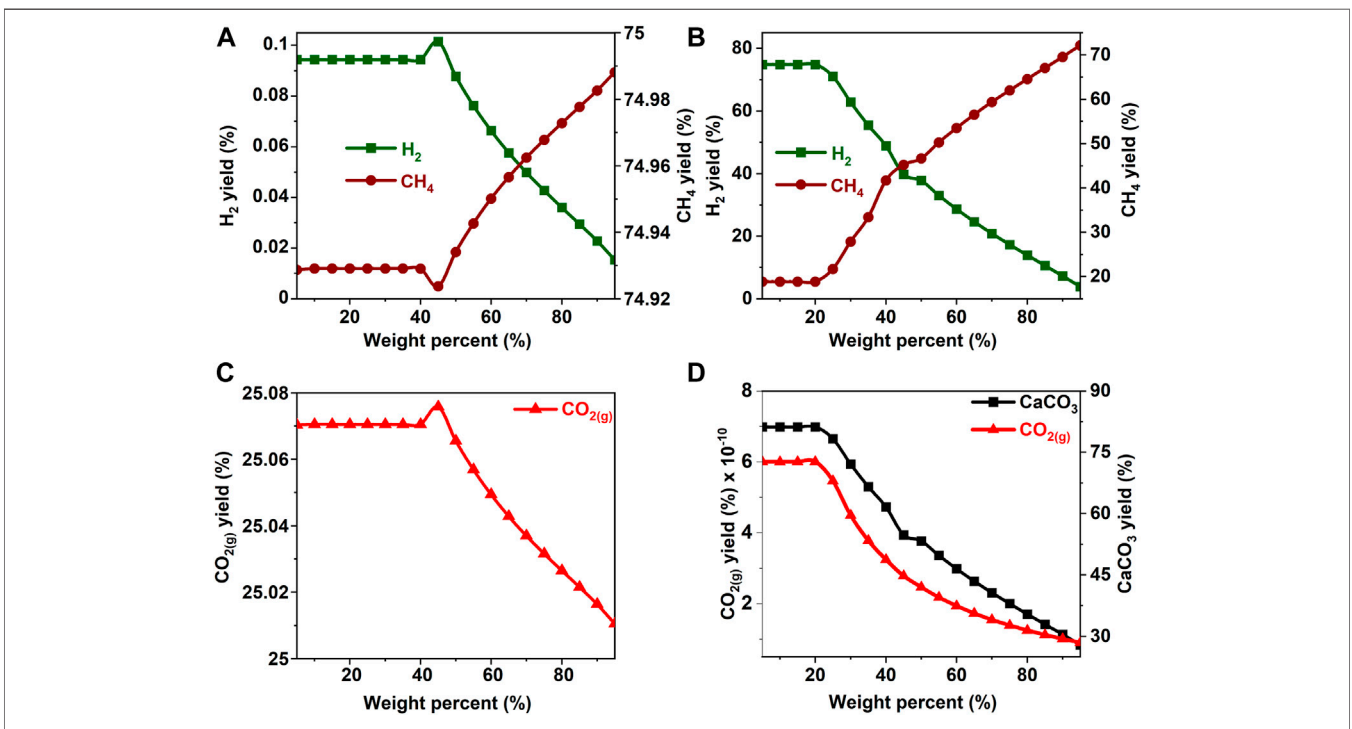
It was interesting to note a significantly lower yield of H<sub>2</sub> at biomass oxygenate concentrations exceeding 60% for all the biomass oxygenates reported in this study which are methanol, ethanol, glycerol, ethylene glycol, acetone, and acetic acid. However, the trends in the concentrations of H<sub>2</sub> and CH<sub>4</sub> at biomass oxygenate concentrations below 60 wt% differ. The effectiveness of using stoichiometric amounts of CaO is evident from the negligibly low concentrations of CO<sub>2</sub> in the gas phase to the order of 10<sup>-12</sup> mol of CO<sub>2</sub> per mole of biomass oxygenate fed after CO<sub>2</sub> capture (**Figures 3D–8D**). At biomass oxygenate concentrations of 20 wt% or less, near complete conversions of CaO to CaCO<sub>3</sub> are noted (**Figures 3D–9D**). In addition to aiding the separation of CO<sub>2</sub>, the heat generated during carbon mineralization aids the water gas shift reaction for enhanced H<sub>2</sub> conversion.

### Effect of Temperature on H<sub>2</sub> Recovery With Carbon Removal

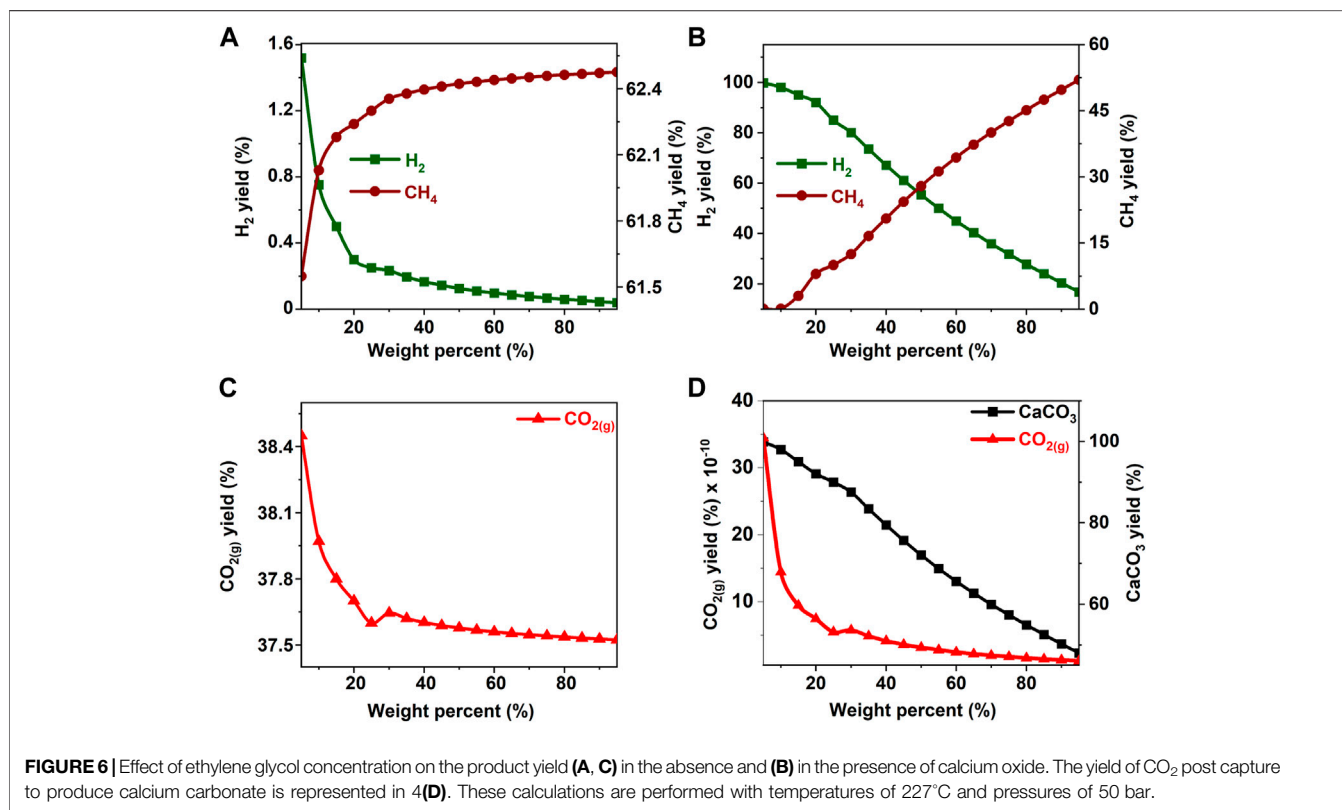
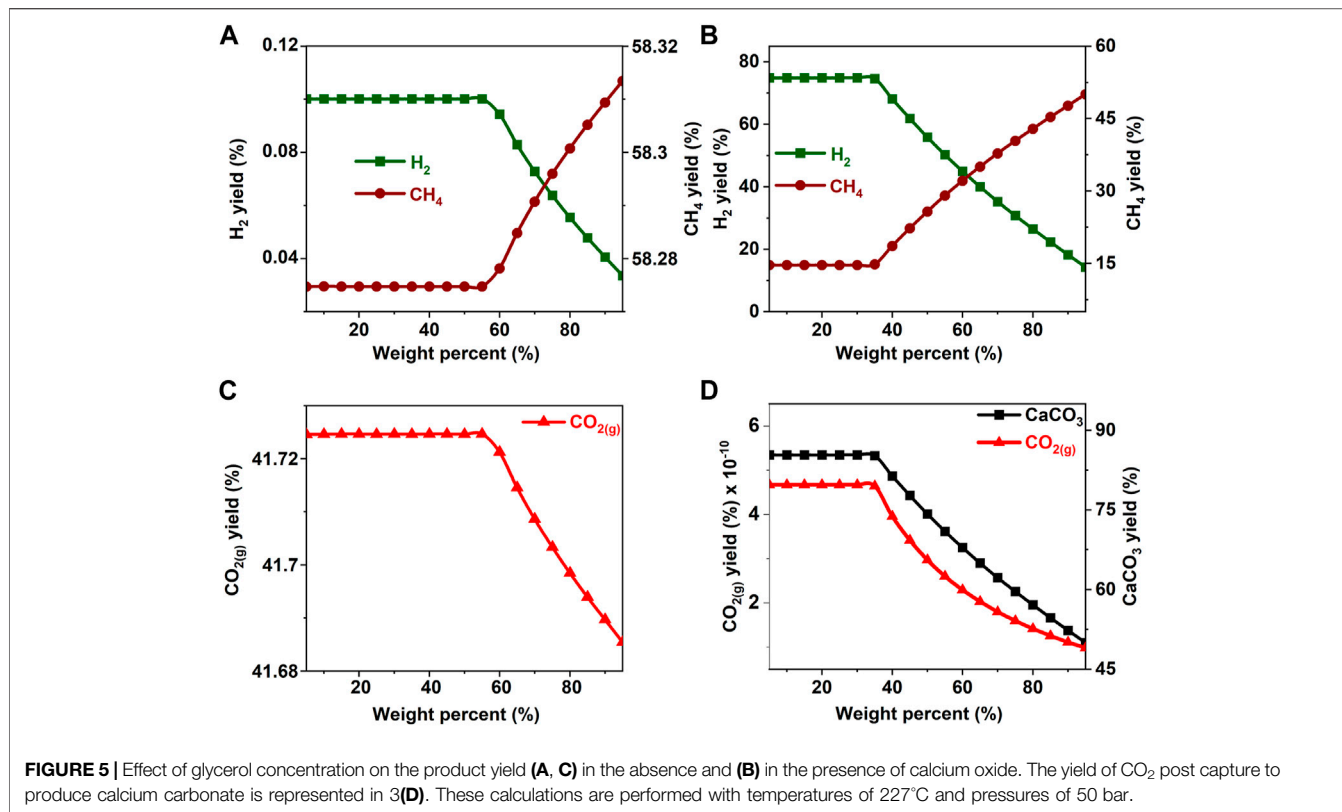
Temperature has a significant effect on coupled multiphase chemical interactions involved in enhanced H<sub>2</sub> recovery with inherent CO<sub>2</sub> removal from biomass oxygenate precursors.



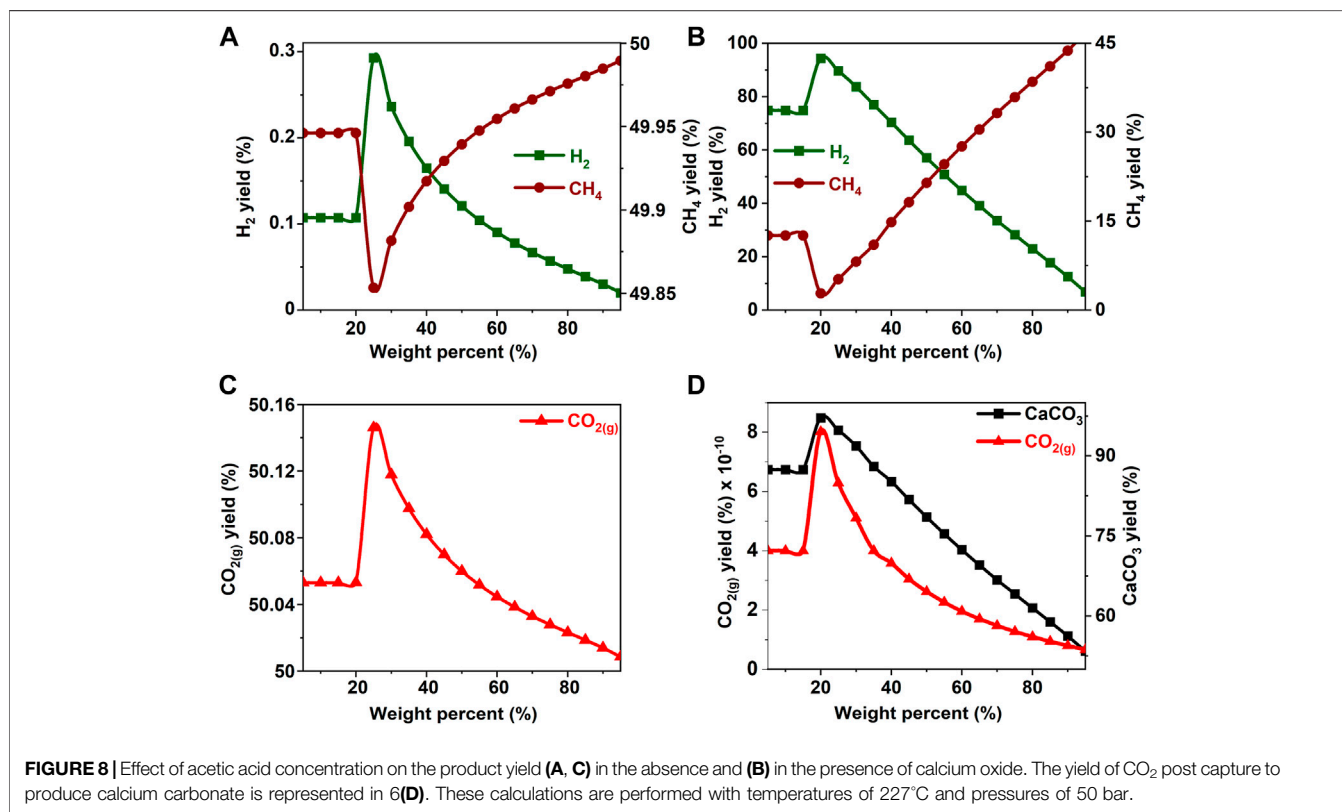
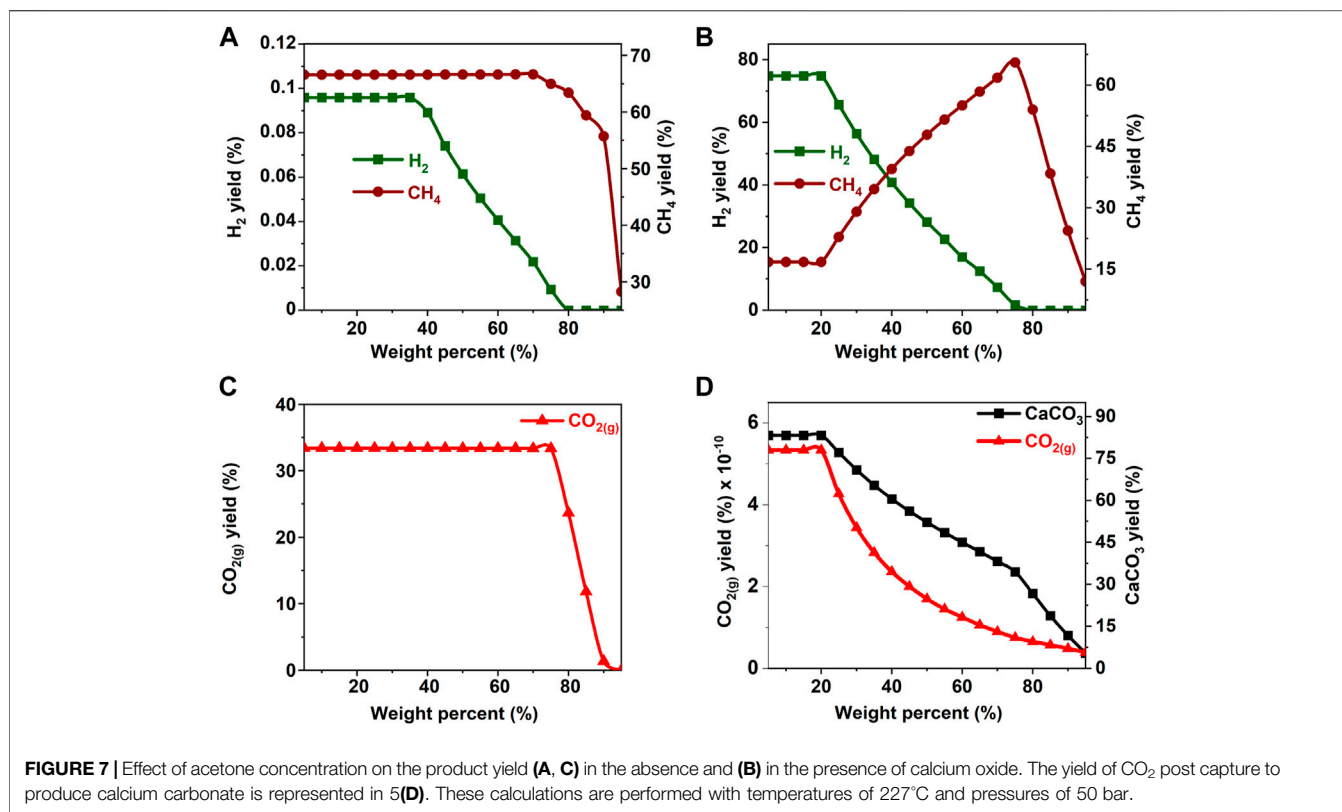
**FIGURE 3 |** Effect of methanol concentration on the product yield (A, C) in the absence and (B) in the presence of calcium oxide. The yield of CO<sub>2</sub> post capture to produce calcium carbonate is represented in 1(D). These calculations are performed with temperatures of 227°C and pressures of 50 bar.

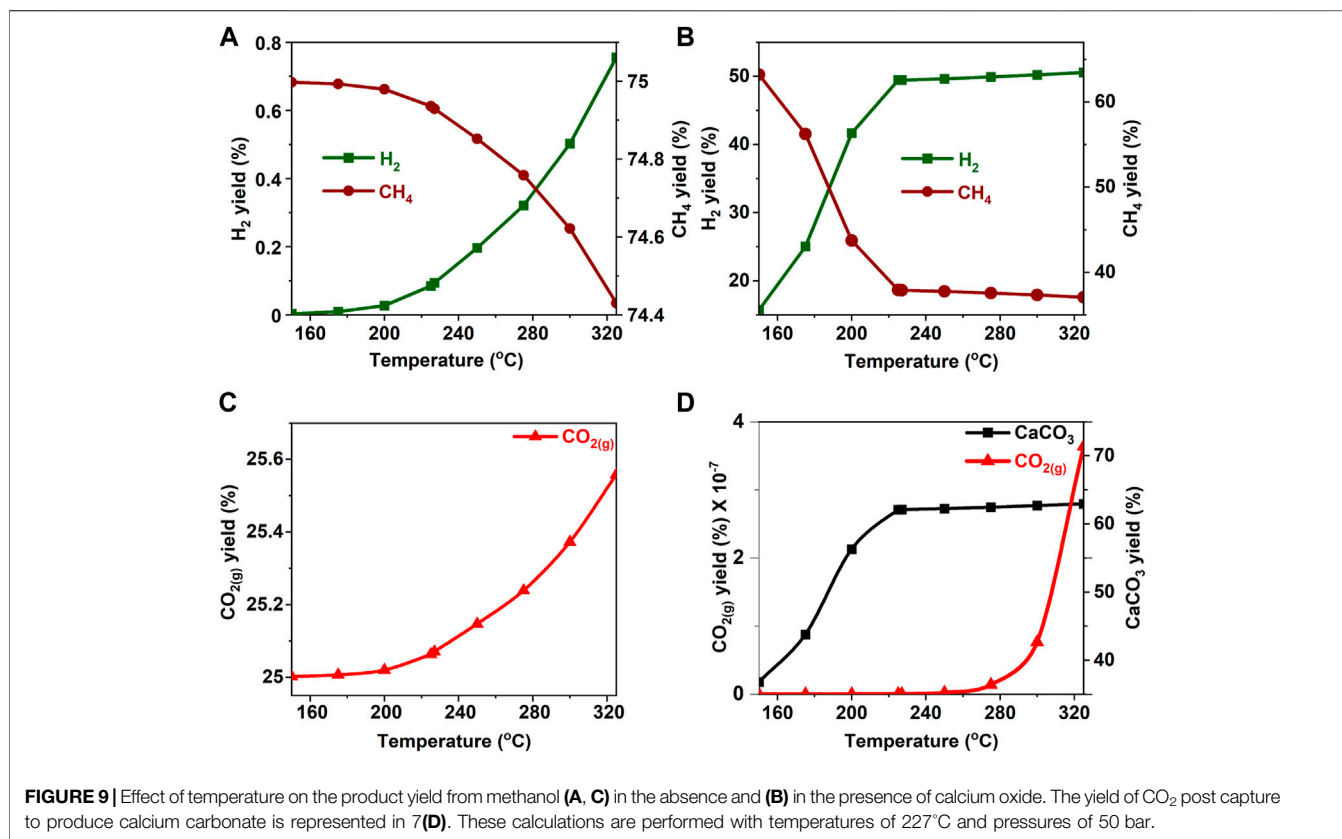


**FIGURE 4 |** Effect of ethanol concentration on the product yield (A, C) in the absence and (B) in the presence of calcium oxide. The yield of CO<sub>2</sub> post capture to produce calcium carbonate is represented in 2(D). These calculations are performed with temperatures of 227°C and pressures of 50 bar.







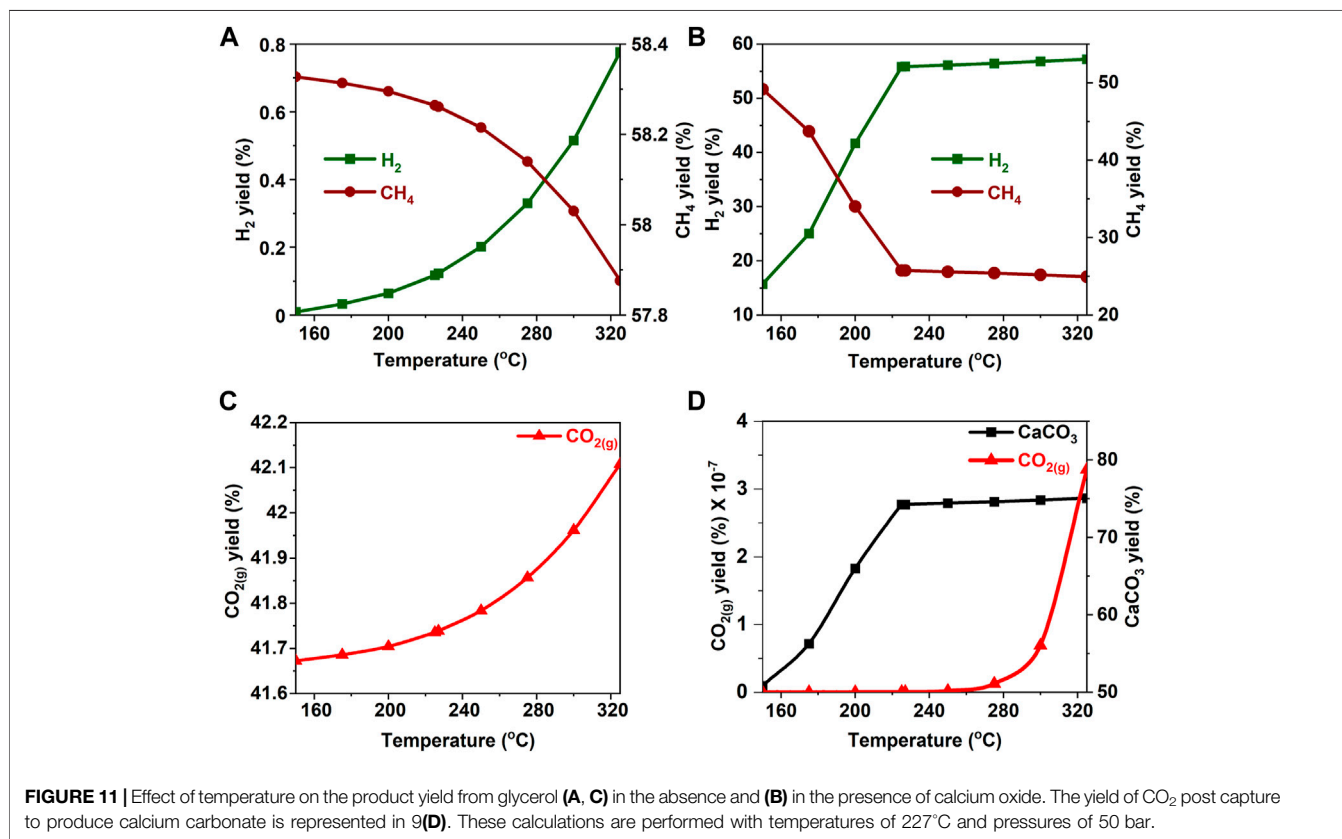
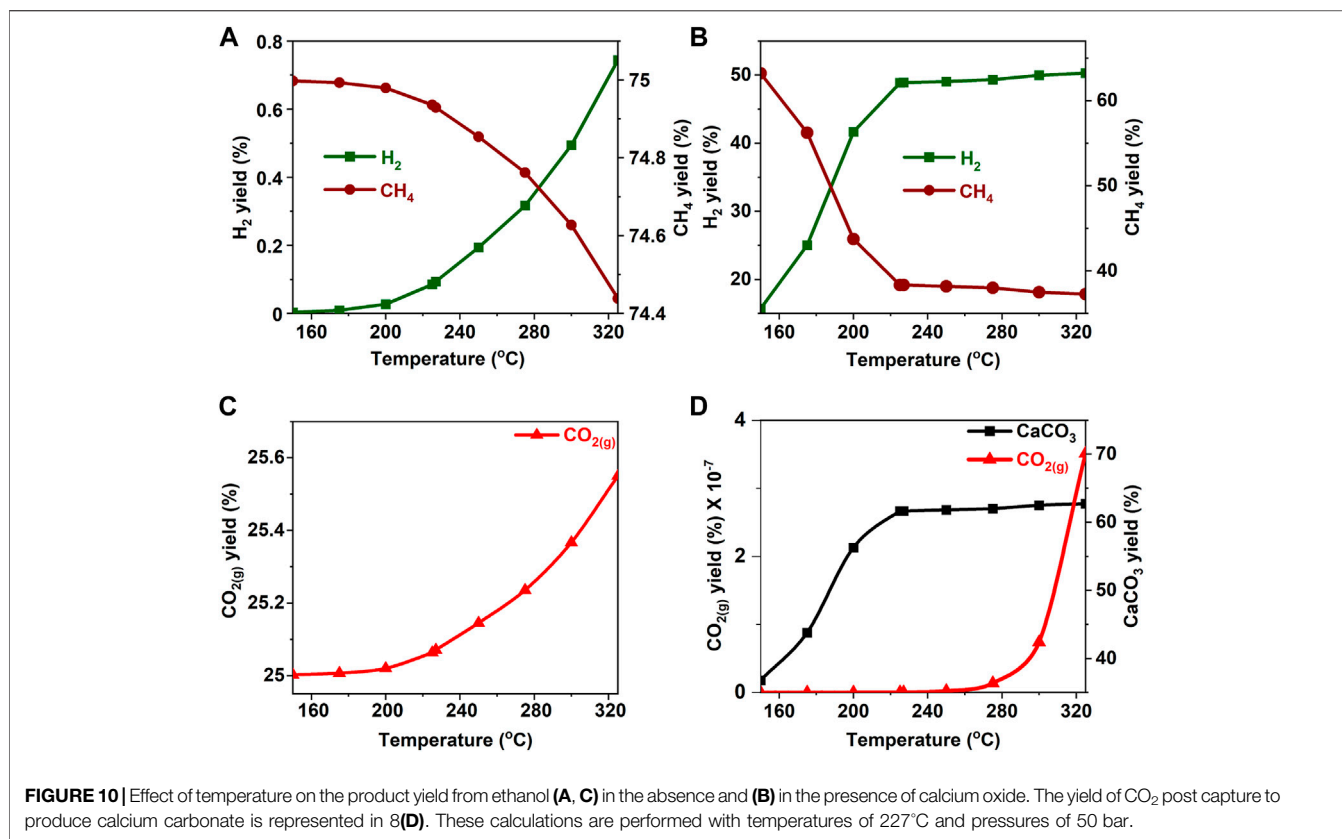


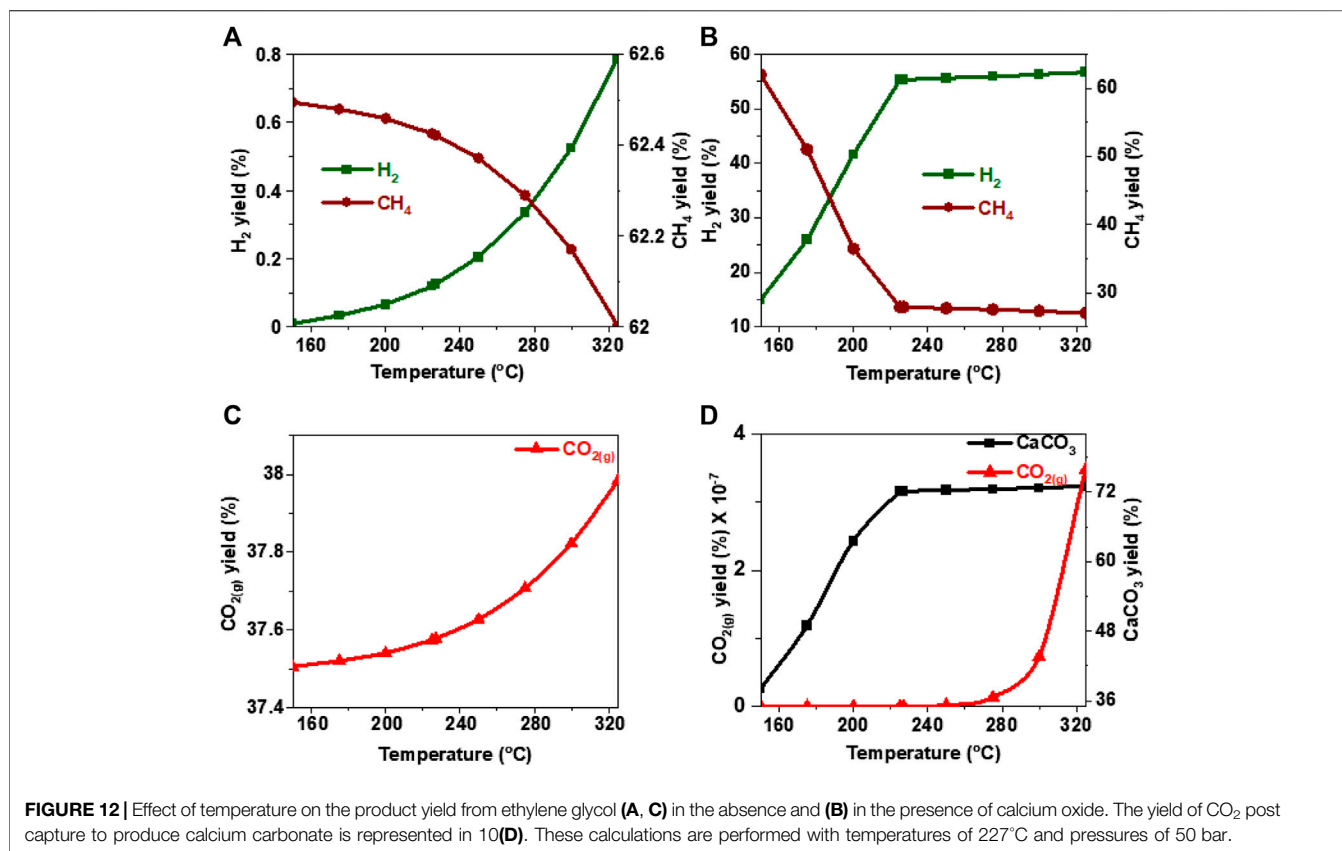
Increase in temperature favors product and reactant formation in endothermic and exothermic reactions, respectively. Further, the solubility of calcium carbonate decreases with temperature which favors the removal of CO<sub>2</sub>. Aqueous biomass oxygenate decomposition is an endothermic reaction (see Reaction 3) and higher temperatures are expected to aid the decomposition behavior. In contrast, the conversion of CO and H<sub>2</sub> to CH<sub>4</sub> is exothermic (and higher temperatures may shift the equilibrium towards the reactants, which favors H<sub>2</sub> yield. Coupling the exothermic water-gas-shift reaction (see Reaction 4) with the carbon mineralization reaction removes CO<sub>2</sub> from the product stream and pushes the equilibrium to the products. This coupling of reactions counterbalances the effect of temperature which is to push the equilibrium towards the products. To investigate the hypothesis that the reaction temperature has a significant effect on enhanced H<sub>2</sub> formation with inherent carbon removal, the gas compositions were determined at temperatures in the range of 150°C–325°C, while all other conditions such as the biomass oxygenate composition and the N<sub>2</sub> pressure were held constant at 50 wt% and 50 bar.

In the absence of a catalyst and CaO for CO<sub>2</sub> capture, H<sub>2</sub> yields are less than 1% for all the biomass oxygenates and CH<sub>4</sub> yields exceed 49% in the temperature range of 150°C–325°C (Figures 9A–14A). H<sub>2</sub> and CO<sub>2</sub> yields increase monotonically with temperature (Figures 9A,C–14A,C). The yields of CH<sub>4</sub> decrease monotonically with temperature at these conditions (Figures 9A–14A). In the presence of CaO for CO<sub>2</sub> capture, H<sub>2</sub> yields of 46–65% or higher are achieved at temperatures

exceeding 220°C. At these conditions, CH<sub>4</sub> yields are 30% or lower at temperatures exceeding 220°C (Figures 9B–14B). These data suggest that alkaline environments (bearing CaO in this case) favor alkaline hydrolysis that contributes to the cleavage of C–C bonds as opposed to acid hydrolysis that results in C–O cleavage which promotes alkane formation. (Davda et al., 2005). Further, CO yields to the order of 10<sup>-3</sup>% and 10<sup>-9</sup>% were noted in the absence and presence of CaO, suggesting that the removal of CO<sub>2</sub> from the gas phase accelerates the conversion of CO to CO<sub>2</sub> (See Supplementary Figure S2A–F).

Unlike the cases without CaO, where we obtained a constant increase in H<sub>2</sub> yield, an asymptotic pattern was observed in cases with *in-situ* CO<sub>2</sub> capture for temperatures greater than 225°C. Furthermore, despite the low amounts of CO being produced, there was a sharp increase CO formation with increasing temperature between 225°C and 320°C. These observations imply that biomass oxygenate decomposition is aided at higher temperatures to produce CO. However, the low concentrations of CO and higher temperatures do not favor product formation in the exothermic water-gas-shift and methanation reactions. These factors contribute to the asymptotic behavior of H<sub>2</sub> above 225°C which also corresponds to the near complete uptake of CO<sub>2</sub> to produce CaCO<sub>3</sub> (Figures 9D–14D). Negligible concentrations of CO<sub>2</sub> to the order 10<sup>-7</sup>–10<sup>-10</sup>% were found in the product gas stream for all cases of biomass oxygenates studied after CO<sub>2</sub> capture using CaO (See Figures 9D–14D).





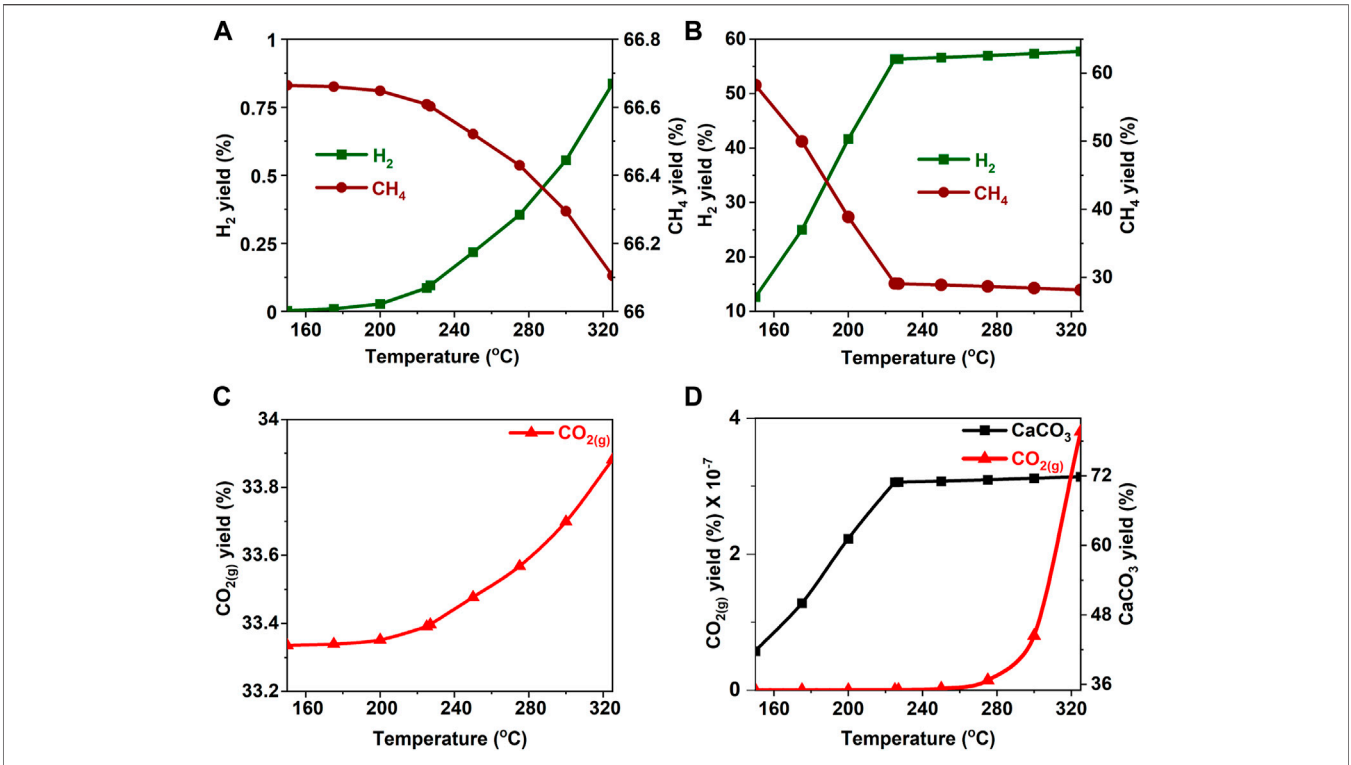
## Effect of Methanation on H<sub>2</sub> Recovery With Carbon Removal

The key limiting factor in accelerating H<sub>2</sub> recovery from biomass oxygenates is the formation of CH<sub>4</sub>. CH<sub>4</sub> is produced from CO or CO<sub>2</sub> and H<sub>2</sub> as building blocks via exothermic reaction pathways (see Reactions 5 and 6). One approach to limit CH<sub>4</sub> formation is to use catalysts that favor C-C bond cleavage and the water gas shift (WGS) reaction over C-O bond cleavage and methanation reactions (Davda et al., 2003; Davda et al., 2005; Coronado et al., 2016). Some examples of these catalysts include rare earth metals supported catalysts such as Pt/SiO<sub>2</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, and Ru/C. Further, catalysts that have a basic character or operate in alkaline environments such as earth abundant Ni catalysts have also been shown to be effective in aiding H<sub>2</sub> evolution (Stonor et al., 2017b).

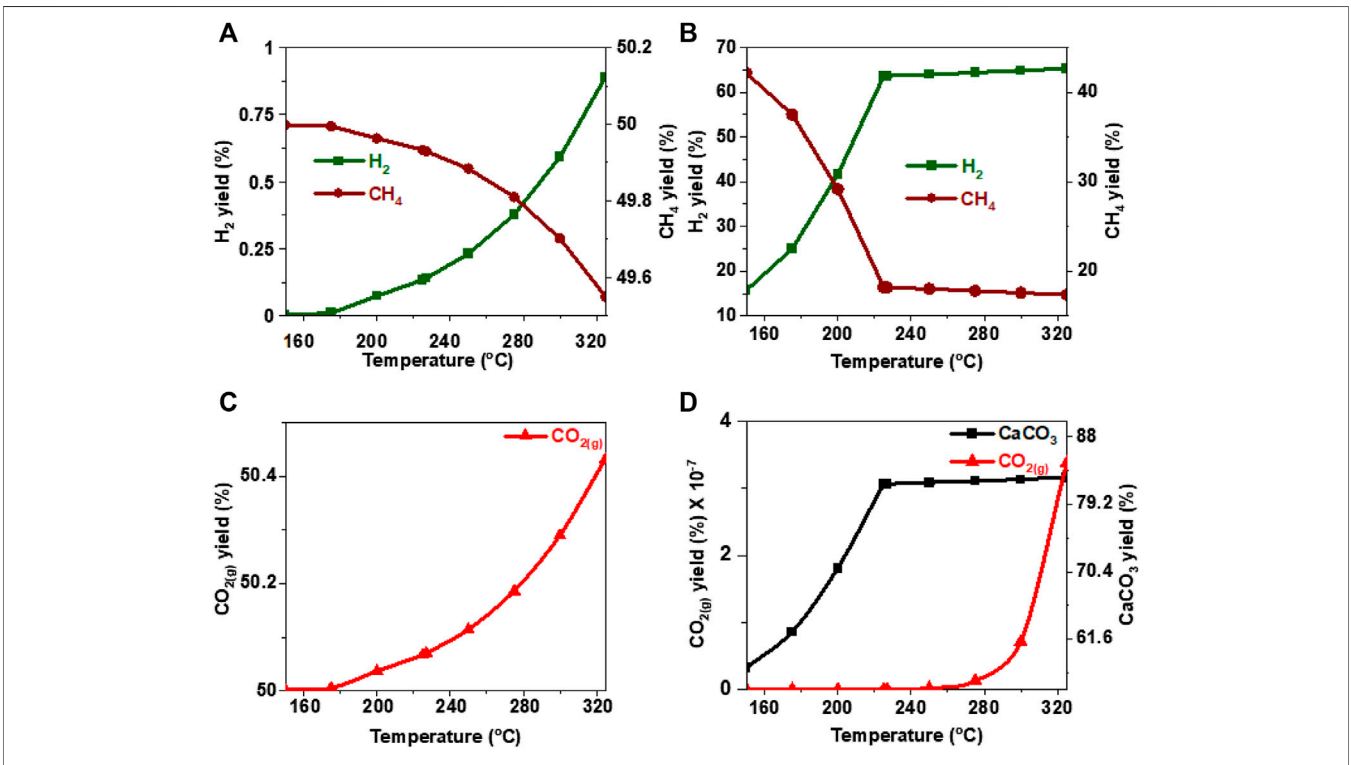
In this study, we build on these observations to investigate the influence of methanation and its suppression on H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, and CaCO<sub>3</sub> yields. In the suppressed methanation case, the reactions associated with CH<sub>4</sub> formation from CO and CO<sub>2</sub> precursors are not included in the model. The studies are conducted at 227°C, N<sub>2</sub> pressure of 50 bar, and biomass oxygenate concentrations of 20 wt%, with and without CO<sub>2</sub> capture. For cases with CO<sub>2</sub> capture, we used a stoichiometric amounts of CaO as defined by (reaction 13). In this study, we consider four scenarios for hydrothermal biomass oxygenate reactions: 1) with methanation, 2) without methanation, 3) alkaline treatment with methanation, and 4) alkaline treatment without methanation reactions (Figure 15).

In the scenario with methanation and without a catalyst, CH<sub>4</sub> and CO<sub>2</sub> compositions are dominant and H<sub>2</sub> yields are less than 0.3%. In the scenario where methanation is suppressed by using a catalyst, H<sub>2</sub> and CO<sub>2</sub> yields are dominant, while CO formation is suppressed and there is no CH<sub>4</sub> observed. For alkaline treatment with methanation, more than 70% conversion of H<sub>2</sub> and CaCO<sub>3</sub>, and substantial CH<sub>4</sub> yields are noted. No CO formation is noted in this case. For alkaline treatment without methanation, H<sub>2</sub> and CaCO<sub>3</sub> are the dominant phases. These results demonstrate that strategies to harness biomass oxygenates for H<sub>2</sub> recovery with CO<sub>2</sub> removal need to incorporate catalysts to suppress methane formation and alkaline sources for *in-situ* CO<sub>2</sub> capture.

Analysis of the product streams provided further insights into the reactivities of various biomass oxygenates. The reactivities of the functional groups proceed in the descending order of OH > COOH > COR. This trend was similar with experimental results obtained by Fu and co-workers (Fu et al., 2020) who investigated the steam reforming of bio-oil and its derivatives and reported the highest H<sub>2</sub> yield from reforming of ethylene glycol, followed by acetic acid, and acetone. Additionally, the separation of CO<sub>2</sub> from the gas phase in the alkaline environment greatly limits methanation kinetically at low and moderate temperatures (less than 227°C) and enhances H<sub>2</sub> production. The lower temperatures are potentially beneficial to catalyst life, and they significantly reduce cost. Furthermore, trace amounts of CO (10<sup>-12</sup> %) were evident in all cases studied, implying that these processes are effective for generating hydrogen with CO content within the 20 ppm limit for fuel cell applications.

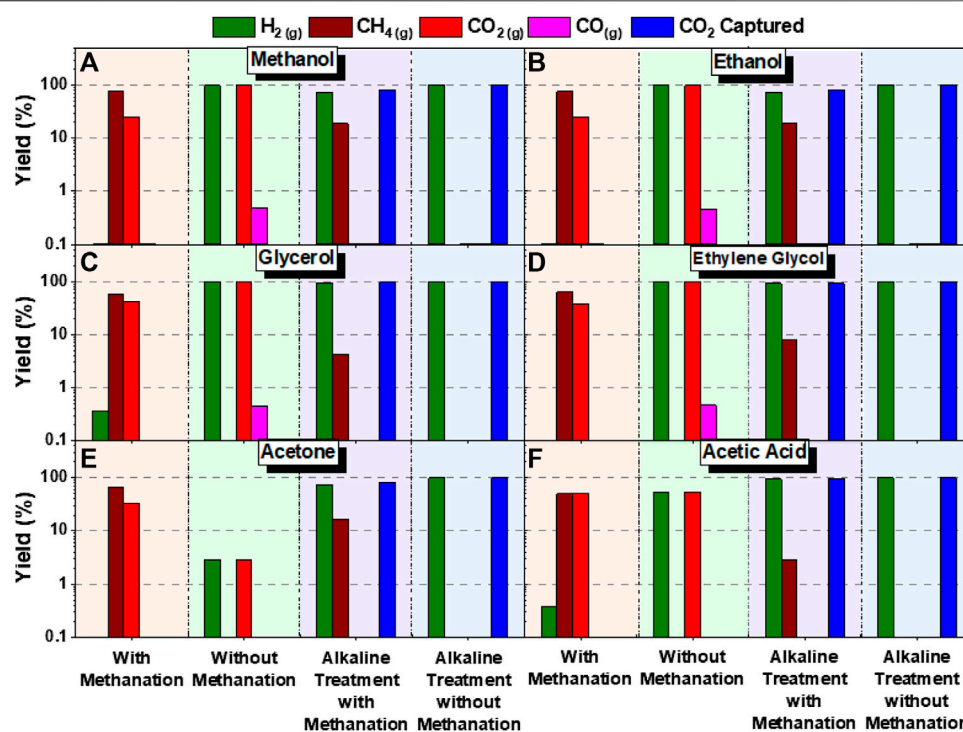


**FIGURE 13** | Effect of temperature on the product yield from acetone (A, C) in the absence and (B) in the presence of calcium oxide. The yield of CO<sub>2</sub> post capture to produce calcium carbonate is represented in 11(D). These calculations are performed with temperatures of 227°C and pressures of 50 bar.



**FIGURE 14** | Effect of temperature on the product yield from acetic acid (A, C) in the absence and (B) in the presence of calcium oxide. The yield of CO<sub>2</sub> post capture to produce calcium carbonate is represented in 13(D). These calculations are performed with temperatures of 227°C and pressures of 50 bar.





**FIGURE 15** | Comparison of theoretical product yields with 20 wt% of (A) methanol, (B) ethanol, (C) glycerol, (D) ethylene glycol, (E) acetone, (F) acetic acid. Thermodynamic product yield was computed for cases with methanation, catalytic effect (without methanation reactions), alkaline treatment with methanation, and alkaline treatment with catalytic effect (without methanation reactions). These calculations are performed with temperatures of 227°C and pressures of 50 bar.

## CONCLUSION

In this study, the thermodynamic limits for enhanced H<sub>2</sub> recovery with inherent CO<sub>2</sub> removal from various biomass oxygenate sources such as methanol, ethanol, glycerol, ethylene glycol, acetone, and acetic acid are reported. The effects of biomass oxygenate-to-water ratio, temperature, and suppression of the limiting methanation reactions on the yields of H<sub>2</sub> and other associated compositions are investigated. As opposed to conventional high temperature reforming processes (> 500°C) at atmospheric pressure, we investigated the effect of maintaining fluids in the aqueous phase on under N<sub>2</sub> pressure of 50 bar and at significantly lower temperatures <325°C. The effect of coupling thermodynamically downhill carbon mineralization reactions for *in-situ* CO<sub>2</sub> capture to enhance H<sub>2</sub> evolution was also studied. Higher H<sub>2</sub> yields with *in-situ* CO<sub>2</sub> capture were achieved with biomass oxygenate concentrations lower than 30 wt%. Water is needed as a reactant for the water gas shift reaction and to facilitate the dissolution of CaO for carbon mineralization. Temperatures around 220–230°C yielded high H<sub>2</sub> conversion with *in-situ* CO<sub>2</sub> capture. Further increases in temperature did not contribute to a significant enhancement in CO<sub>2</sub> capture. The suppression of methanation reactions and *in-situ* CO<sub>2</sub> capture to produce inorganic carbonates is crucial for producing high purity H<sub>2</sub> that can be used in a fuel cell. The thermodynamic feasibility of these reaction pathways demonstrates that low value residues such as Ca-rich alkaline residues and wastewater streams bearing biomass oxygenates can be successfully upcycled to produce high value H<sub>2</sub> with inherent CO<sub>2</sub> removal.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

## AUTHOR CONTRIBUTIONS

PO conducted the analyses and completed the initial draft. CB and RK contributed to the resource assessments. GG conceptualized the study and contributed towards writing and editing.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenrg.2021.742323/full#supplementary-material>

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