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# Thermodynamic analysis of syngas production and carbon formation on oxidative steam reforming of butanol

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## ABSTRACT

Theoretical calculations of chemical equilibrium were adopted to explore the syngas production of oxidative steam reforming of butanol (OSRB). The results indicated that when the  $H_2O/C_4H_9OH$  molar ratio was 3 and the  $O_2/C_4H_9OH$  molar ratio was 1.5, the thermal neutrality temperature reached 602 °C, generating a corresponding  $H_2$  yield of 59.3%, a CO yield of 39.5%, and reforming efficiency of 65.1%. Additionally, when the OSRB was at moderate temperatures (400–800 °C), adding an appropriate amount of  $O_2$  effectively inhibited coke formation and exerted only a minor effect on butanol reforming efficiency. The analysis of the coking boundaries indicated that at the same  $H_2O/C_1$  molar ratio, alcohol fuels with higher carbon numbers (butanol > ethanol > methanol) produced higher degrees of coke formation. However, if OSRB was used, the amount of  $H_2O$  and  $O_2$  addition was able to be controlled to inhibit coke formation and reduce the coke formation zone considerably.

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## Introduction

The imminent exhaustion of the fossil fuel supply and the need for environmental protection have engendered the development of clean energy sources to be a worldwide concern. The transportation industry is the primary source of carbon emissions all over the world; as a result, a critical focus of research and development is the use of alternative fuels to partially replace fossil fuels for automotive engines. Since the 1970s, ethanol has been the primary alternative fuel used in

automotive engines to gradually reduce dependence on fossil fuels. Long-term testing has revealed many deficiencies in the practical use of ethanol. Ethanol is water-soluble and relatively corrosive, which substantially affects the durability of automotive applications. In recent years, a breakthrough in the production technology of biobutanol was made. The characteristics of butanol was the following advantages: 1) It has double the amount of carbon of ethanol, a higher heating value, longer carbon chains, and lower polarity; these characteristics, compared with those of ethanol, make butanol more suitable for mixing with gasoline; 2) the Reid vapor

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pressure of butanol is 0.33 psi, which is much lower than that of gasoline at 4.5 psi or that of ethanol at 2.0 psi, and is therefore safer than both; and 3) butanol is less corrosive than ethanol is. The value of butanol as an alternative fuel for automobiles has been proven repeatedly; therefore, the development of technology that using butanol is urgently required. Although the number of studies regarding the application of butanol is limited, most have thus far pertained to its use in spark ignition engines or hydrogen production through butanol reforming; however, some studies have involved its use in solid oxide fuel cells [1–3]. Currently, the majority of research into butanol has focused on blended combustion in automotive engines. For example, Yang et al. [4] explored the feasibility of adding 1-butanol to gasoline for use in automotive engines. The test results revealed that when a fuel mixture contains less than 20% 1-butanol by volume, engine power is maintained, and no engine modification is required. Wasil et al. [5] explored the pollutant emissions of 1-butanol as a fuel additive in marine two-stroke engines. The results revealed that emissions and engine power after adding 1-butanol at 20% by volume and ethanol at 10% by volume to gasoline were relatively close. Compared with adding the same percentage of ethanol, adding butanol resulted in lower HC, and CO emissions, but slightly higher NO<sub>x</sub> emissions. Deng et al. [6] studied engine performance and operational parameters when 35% butanol by volume is blended with gasoline, and the throttle is fully open. The results showed that adding butanol allows for advancement of the ignition timing without obvious knocking and can improve engine performance, fuel consumption rates, and HC and CO emissions, but is not beneficial regarding NO<sub>x</sub> emissions. Accordingly, the technology of hydrogen production from butanol reforming can improve these results. The reforming process can fully utilize engine waste heat to produce combustible, highly concentrated hydrogen-rich syngas. Hydrogen-rich syngas is composed mainly of H<sub>2</sub> and CO, in which H<sub>2</sub> has a high flame propagation speed, and CO has a relatively high adiabatic flame temperature. Therefore, if an optimal feed-stock ratio can be determined, substantially lowering pollutant emissions can be anticipated, thereby improving engine thermal efficiency and expanding the lower flammability limit (LFL).

To date, the use of engine waste heat for hydrogen production through automotive butanol reforming has been relatively rare. Internationally, related studies have included that of Fennell et al. [7], who applied thermochemical energy recovery technology to gasoline direct injection technology. The experimental results indicated that reformed exhaust gas recirculation technology applied to the original fuel system improved engine combustion efficiency, leading to lowered CO<sub>2</sub> and particulate matter (PM) emissions and greatly decreased NO<sub>x</sub> emissions. Ji et al. [8] investigated steam reforming of ethanol (SRE) aided by engine waste heat, and reported that when the syngas volume fraction reached 2.43% of the total intake gas, the indicated thermal efficiency increased from 34.52% in the original engine to 39.01%, and HC and NO<sub>x</sub> emissions decreased as the syngas volume fraction increased. These studies have demonstrated the benefits of syngas in automotive combustion engines. Therefore, if butanol is reformed before it is fed as a blended fuel for

combustion, this could significantly improve engine power and pollutant (e.g., HC, NO<sub>x</sub>, or PM) emissions, leading to enhanced energy utilization efficiency.

In research regarding hydrogen production from butanol reforming, Cai et al. [9] observed that bimetallic catalysts resulted in higher butanol conversion efficiency and higher hydrogen concentration and prevented catalytic deactivation. Catalysts with Rh (Co–Rh/ZnO) exerted the optimal catalytic effect, producing the least amount of coke. Cai et al. [10] further explored the use of bimetallic catalysts in hydrogen production from oxidative steam reforming of butanol (OSRB). They identified that Co–Ir/18CeZrO<sub>2</sub> exerted the optimal catalytic composition, and this catalyst inhibited surface sintering and coke formation. Cai et al. [11] used steam reforming of butanol (SRB) to investigate the behavior of Co-based catalysts in hydrogen production and observed that the Co–Ir/ZnO catalyst yielded maximum hydrogen production. In addition, Raman analysis results indicated that adding Ir to the catalyst prevented coke formation on the catalyst. Bimbela et al. [12] explored the use of Ni–Al catalysts in H<sub>2</sub> production through the steam reforming (SR) of 1-butanol and acetol. Parameter settings in the study (i.e., reforming temperature 750 °C, gas hourly space velocity 57,000 h<sup>-1</sup>, and Ni content 23%) resulted in a fuel conversion rate of 99.05%, showing butanol's innate resistance to coke formation.

In studies of theoretical calculations, Huang et al. [13] used the method of the minimum of Gibbs free energy in thermodynamics analysis to explore H<sub>2</sub> production from partial oxidation of butanol (POXB). They observed that temperatures near 700 °C or above with O<sub>2</sub>/C<sub>4</sub>H<sub>9</sub>OH = 1.5–2.0 resulted in higher H<sub>2</sub> yields. Nahar and Madhani [14] also used the free energy minimization method of thermodynamics to analyze syngas production through SRB. Optimal parameters were determined to be reforming temperatures between 600 °C and 800 °C and H<sub>2</sub>O/C<sub>4</sub>H<sub>9</sub>OH molar ratios between 9 and 12. These conditions generated maximum syngas production rate, with yields of H<sub>2</sub> between 75.13% and 81.27% and CO between 65.48% and 55.57%. Wang and Cao [3] also used the minimum of Gibbs free energy in thermodynamics to explore partial oxidation of butanol and found that the optimal conditions for H<sub>2</sub> production were at reaction temperatures between 1115 and 1200 K with O<sub>2</sub>/C<sub>4</sub>H<sub>9</sub>OH molar ratios between 1.6 and 1.7. Under optimal conditions, H<sub>2</sub> yields of 93.07%–96.56% and CO yields of 94.02%–97.55% were achieved with no coke formation.

The review of literature focused on butanol reforming revealed that most studies can be categorized as adopting either experimental methods or thermodynamic analyses. Experimental method studies have primarily focused on the preparation of catalysts, and thermodynamic analyses have focused on SRB or POXB. Neither category of study has addressed the OSRB reactions that are most appropriate for automotive use. In OSRB reaction process, it could provide the energy required for a self-sustaining reaction by using the heat release of oxidation, and carbon deposition may also be avoided with the appropriate addition of oxidants. Therefore, the objective of this study was to analyze OSRB parameters [e.g., reaction temperature, water-to-butanol (H<sub>2</sub>O/C<sub>4</sub>H<sub>9</sub>OH) molar ratio, and oxygen-to-butanol (O<sub>2</sub>/C<sub>4</sub>H<sub>9</sub>OH) molar ratio] using butanol as the alternative fuel of automobiles for on-

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