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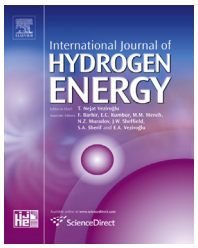

Feasibility analysis of H_2 production by calcium looping process based on coal gasification in a transport reactor

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ABSTRACT

Calcium looping process (CLP) is one kind of carbonaceous material gasification process applied in the H_2 rich syngas production and CO_2 separation. In this research, a transport reactor with efficient heat and mass transfer and better gas and solid mixing was applied as the gasifier to produce H_2 rich syngas with in situ CO_2 capture. The primary objective of this research was to investigate the feasible operation conditions for gasifier and entire looping process. The gasification process was analyzed by model based on the reactor hydrodynamics and chemical kinetics. Influences of operating parameters, i.e. temperature, steam to carbon ratio and pressure, on the reactor hydrodynamics, reaction rates and conversion ratios, syngas flow and compositions, steam and power consumption were given and discussed. Feasible operation conditions for gasifier and system configuration were proposed according to the heat and power balance, H_2 yield and systematic energy conversion efficiency. Simulation results indicated that feasible operation with H_2 and power co-production can be achieved with the gasification temperature of 1273 K, pressure of 0.9 MPa, steam to carbon ratio of 1.8 and CaO to carbon ratio of 1.0. For this feasible operation, the H_2 output exceeded 0.78 Nm^3 per kg coal and energy conversion efficiency was higher than 40%.

Introduction

Calcium looping process (CLP) is one kind of carbonaceous material gasification process which can be applied for the production of the H_2 rich syngas with in situ CO_2 capture. It features steam as the gasification agent and CaO as a sorbent to absorb the CO_2 which produced during the gasification. The introduced CaO also plays the role of heat carrier which provides the necessary energy for the endothermic gasification reactions.

The concept of H_2 production can be traced back to the "CO_2 acceptor process" proposed by Curran [1]. In this process, CO_2 is absorbed by CaO via carbonation reaction in a gasifier and $CaCO_3$ is decomposed to CaO and CO_2 via calcination reaction in a regenerator. Based on this concept, typical coal based H_2 production systems coupled with in situ CO_2 capture have been proposed in recent years, including ZECA zero emission coal technologies [2], NEDO HyPr-RING [3], CLP of the Ohio State University [4], GE EER's AGC (advanced gasification-combustion) process [5], AER (absorption enhanced

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reforming) process of the Vienna University of Technology [6], LEGS (lime enhanced gasification) of the University of Stuttgart [7], near zero emission coal utilization systems proposed by Wang [8], Esmailia [9] and Chen [10]. Although there are still challenges to its commercial application, such as attrition and cyclic reactivity of CaO based sorbents, sorption kinetics, the eutectic problem of calcium based compound system and sintering of $CaCO_3$ etc, the technique is quite attractive. It has the capability of producing H_2 rich syngas with in situ CO_2 capture. In literature, models based on thermodynamic equilibrium have been applied widely to predict the gasifier performance. This approach can predict the theoretical gasification or thermal efficiency that could be attained within the gasifier for a given feed stock. Influences of operating variables, such as pressure, temperature, steam to carbon ratio and CaO to carbon ratio, on the gasification behavior and product compositions were systematically examined and analyzed [8–17]. Results based on thermodynamic analysis showed that H_2 is the primary product gas. CaO is partially carbonated to $CaCO_3$ by absorbing CO_2 that generated by WGS occurring in the char-CaO-H_2O system. Because of the selective removal of CO_2, the reaction equilibriums are shifted to the products side and more hydrogen is produced. The maximal H_2 concentration is near 80 vol%. The remaining is composed of CH_4 and very small proportions of CO_2 and CO. CO and CO_2 keep increasing with the temperature. The capture of CO_2 is intrinsically favored by the increase of pressure. H_2 and CH_4 contents increase with the increment of system pressure. The addition of more CaO into reactor is beneficial to capture more CO_2. But when CaO/C_{coal} is greater than 1, its effect on CO_2 capture becomes less. Studies published in literature show that the optimal CaO/C_{coal} is around 1.

In order to predict the kinetically controlled processes, equilibrium models are modified and kinetics models are developed. Esmailia [9] proposes a method for modifying the thermodynamic equilibrium model. The presented method includes the introduction of an approach temperature which corresponds to the deviation from equilibrium condition. Comparison with experimental measurement reveals that the modification of the equilibrium model has significantly reduced the predicted error in the product gas composition. Kinetics models provide essential information on the kinetics mechanisms to describe the conversion during gasification, which is crucial in designing, evaluating and improving gasifiers. Inayat [18,19] presents kinetics model and predicts that the H_2 concentration can be increased from 65% to 85% with the addition of CaO sorbent for biomass gasification. It was reported that the temperature has more influence on the hydrogen yield than the steam to biomass ratio [19]. With more detailed consideration of the pyrolysis and tar cracking stages, Sreejith [20] proposes a reaction kinetics model for air-steam fluidized bed gasification of wood with in situ capture of CO_2. The effect of operating conditions such as equivalence ratio, temperature, steam to biomass ratio and sorbent to biomass ratio on the gasification performance are evaluated. More sophisticated carbonator models have been reported by taking into account the hydrodynamics characteristics of fluidized bed. Kinetic models of carbonation process for capturing CO_2 from post combustion flue gas have been reported [21–26]. Meanwhile, H_2 production experiments have also been widely performed using a fixed bed, moving bed and bubbling/circulating fluidized bed reactors [8,14,27–35].

From the above extensive research, predictive models and interesting results on gasifier performance and CLP were obtained. However, most of them are focused on either a bubbling fluidized bed or fixed bed gasifier. In recent years, transport reactor [36] has attracted much interests. It is an advanced gasification technology with efficient heat and mass transfer and better gas and solid mixing. It is characterized by a fully developed flow pattern, higher throughput per cross-sectional, flexible coal applicability and load following capability. Similar to the gasification process of fluidized bed and entrained bed reactor, coal together with O_2 or air and steam are fed into the transport reactor. The transport reactor is operated with the same exit temperature as a fluid bed reactor but with shorter solids residence times, approximately 5–30 s using particles 100–300 um in diameter [36]. Although it has some drawbacks, such as lower thermal efficiency, particulate carryover, problems in gas solids separation and be limited to non-caking coals due to agglomeration, it is suitable for many Chinese coals. These coals usually have higher sulfur and ash content. Besides, the melting points of them are also high. Theoretical and experiment research has been given and focused on the study of hydrodynamic [36] and kinetics mechanism in the reactor [37], gasification process modeling and rig design by experiment [37,38]. The results show that the gasification reactor can have a carbon conversion of approximately 95%. The transport gasifier has been manufactured by Kellogg, Brown and Root (KBR) and applied to produce syngas in Mississippi 600 MWe IGCC power plant.

Apart from producing syngas, a transport reactor has the potential in to produce hydrogen rich gas with in situ CO_2 capture. But its feasible operation conditions and corresponding system performance, such as H_2 yield, energy conversion efficiency, hydrodynamic parameters, etc, are still under investigation. The difference of hydrogen production applications with existing gasification cases can be expressed as follows.

1 Chemical reactions and components involved are different. In the case of hydrogen production, no oxygen is fed to gasifier and the combustion of char and other combustible species are eliminated. On the other hand, a large amount of CaO particles is fed to the gasifier to capture CO_2 and H_2S. CaO reacts with CO_2 to form $CaCO_3$. Sulfur is absorbed by CaO to form CaS. Thus, solid components of CaO, $CaCO_3$ and other related calcium compounds would be included in the process. Due to the integration of pyrolysis, gasification and carbonation reaction in one reactor, CO_2 generated can be captured in the process of carbon conversion. CO is converted to CO_2 and H_2 via shift reaction. Its content can also be decreased to a low level. Methane is assumed to be produced by pyrolysis and reaction R3. Due to the low reaction temperature, reaction rate of reaction R5 is very small, much of methane is left in syngas. Thus, syngas produced in this process is mainly composed of H_2 and CH_4. CO and CO_2 content can be reduced greatly. Volumetric flow of the syngas is greatly decreased due to CO_2 capture, while H_2 content can be increased up to 60%. Solid components involved are char,