Coal-to-Methanol Process: Progress Report 2

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Abstract

A Shell coal gasification process and a high-temperature CO shift reactor will be used in order to produce 5,000 MT of methanol per day. A gasifier has been simulated in ASPEN in order to determine preliminary operating conditions upstream of the methanol synthesis process. Coal, oxygen, and steam were fed into the gasifier at 220, 120, and 80 MT/hr, respectively. Under these specifications, the resulting CO gas will require a 41% conversion to H_2 in a water-gas shift reactor in order to produce the desired output of methanol. Furthermore, the ~84 kmol/hr of H_2S in the syngas effluent will be removed via a Rectisol process, and subsequently converted into sulfuric acid in the Claus and wet catalysis processes; the final output may be sold for profit. The product ash from the gasifier may also be sold for use in roadfill or concrete.

Introduction

Entrained-flow gasifiers are capable of gasifying low-quality coal feedstock into clean, tar-free syngas at the expense of a relatively high oxygen consumption. There are several well-established processes within this branch of gasification technology, several of which are examined in *Gasification*.[1] Dry-coal gasifiers have the advantage of operating with a minimum amount of blast, approximately 20-25% less oxygen, as opposed to a coal-water slurry feed system. Any method of lowering the oxygen consumption for the already blast-intensive entrained-flow reactor is desirable. According to literature, adding a second stage to a dry-feed gasifier increases both the complexity and steam consumption for a corresponding 1% rise in efficiency; the incremental efficiency gain of this added stage is not economically feasible. Of the processes examined, the Shell and Noell gasification systems are most appropriate for the desired application. Although the two systems share many characteristics, the relative abundance of information regarding the Shell coal gasification process (SCGP) boosts its appeal.

A gasifier has been modeled in ASPEN Plus as an aggregate of three components: a decomposition block, an equilibrium reactor, and a cyclone separator. In order for downstream calculations involving the components of a nonconventional solid, ASPEN requires the decomposition of coal into its constituents; this is accomplished by the first block. The decomposed coal then enters an equilibrium reactor where it is blasted with oxygen in order to model the actual gasification reaction. Solid and vapor components are then split to simulate the physical geometry of the gasifier.

The resulting syngas is comprised primarily of H_2 and CO, with notable amounts of H_2O and CO_2, and small amounts of H_2S and N_2. Despite the low concentration of H_2S, its removal is vital to the function of the downstream water-gas shift reactor, as it poisons the catalyst used. Furthermore, it is an impurity in the final methanol product and an environmentally unacceptable emission. A selective acid gas removal (AGR) process will be utilized to separate the fuel syngas from the sour gas; the H_2S will then be converted to sulfuric acid via a number of successive oxidations and a hydrogenation.

The methanol synthesis stoichiometry calls for a 2:1 ratio of H_2 to CO; the gasification process generally does not produce this molar ratio. A water-gas shift reactor is therefore necessary upstream of methanol synthesis as a precursor. The results of the gasification simulation provide a meaningful estimate of the required conversion and consequent operating temperature of the CO-shift reactor.

A block flow diagram of the overall methanol synthesis process may be found in Appendix 1.

Results

Based on the analysis of various entrained-flow gasifiers as summarized in Appendix 1, the SCGP was selected as the preferred system for coal gasification. The coal is fed through four burners symmetrically positioned at the bottom of the reactor, where it is blasted with oxygen. Gasifier operating conditions are typically around 1500°C and 30-40 bar. The slagging ash exits the bottom of the cylinder, where it is quenched by a water bath. The gasifier effluent is cooled to 900°C first with a recycle gas stream, followed by a single syngas cooler to 280°C. Half of the syngas is further cooled and exits the gasification process, while the other half is recycled for use as a quench gas.

An ASPEN simulation modeling a general gasification system was used to obtain preliminary results of gasifier conditions and effluent. Dry coal was fed into the system at 25°C, 1 bar, and 220 MT/hr, while O_2 was fed at the same temperature and pressure, with a flow rate of 120 MT/hr; the gasifier pressure was 35 bar. Saturated steam at system pressure was also fed into the gasifier at 80 MT/hr. At these specifications, the outlet flow rate of CO gas was 11.0 Mmol/hr, the H_2 gas flow rate was 8.54 Mmol/hr, and the solid ash left the column at 33,000 kg/hr. The gas outlet also contained significant amounts of H_2O, CO_2, and H_2S (83.7 kmol/hr). The outlet temperature of the gasifier was 1070°C.

Discussion

The PR-BM base method is appropriate for modeling coal gasification and combustion, and was therefore chosen as the thermodynamic package for the ASPEN simulation. Coal feed was inputted based on the dry basis analyses. Because much of the design is specified by the choice of gasifier, the salient information lies in the flow rates of feed and effluent. With this in mind, the behavior of the relevant variables, specifically the inlets of coal, oxygen, and steam, were adjusted in order to optimize the product streams. The costs of coal and oxygen feedstocks differ by ~4%; thus they are economically interchangeable within the design. A total of approximately 6,502 kmol/hr of CO is necessary to meet the desired 5,000 MT/day production of methanol. Since H_2 can only be obtained via the water-gas shift, the total sum of CO and H_2 leaving the reactor must total about 19,506 kmol/hr in order to still meet the quota after adjustment to a 2 H_2 to 1 CO ratio. Minimizing the sum of the coal and oxygen inlets while maintaining the combined 19,506 kmol/hr outlet of H_2 and CO was therefore the primary design criterion.

Because the gasification reaction is highly exothermic, steam is fed in order to quench the gasifier, maintaining operating temperature. Steam also increases H_2 and CO production, as it is broken down into its components at the gasification conditions. Remaining H_2O will react downstream in the CO shift reactor, decreasing the necessary water feed rate for that step.

Acid gas in the form of H_2S must be removed from the syngas not only because it is a poison to the catalyst in the water-gas shift reactor, but also because it is a contaminant in the methanol product and environmentally dangerous. At the specified feed rate of coal, the H_2S content is approximately 64 ppmv. A Rectisol process, utilizing cold methanol as the solvent, is capable of removing sulfur components to a sub-ppm level. It also offers a high selectivity for H_2S relative to CO_2 (1:9.5)[1] thus meeting specifications for both gas purity and selectivity. An operating temperature in the range of -30 to -60°C is responsible for methanol's high absorption and consequently effective removal of H_2S. The recovered sulfur may then enter a Claus process, after which it will undergo wet catalysis, where it is converted into sulfuric acid by a series of oxidation and hydrogenation reactions.

The results of the ASPEN simulation have been used to assess the conditions of downstream blocks. In particular, the ratio of H_2 to CO must be shifted to 2:1; this requires a 41% conversion of CO in the water-gas shift reactor. Because HTS reactors can typically achieve 75-80% conversions under normal operating conditions, the system only requires one reactor in the water-gas shift unit, an HTS operating at high temperature. Although a high temperature for this unit is economically unfavorable, the conditions here are set by the gasifier, whose design is much more sensitive to economic considerations.

Conclusion

A preliminary assessment of the operating conditions for the gasification process and CO shift reactor have been determined via an ASPEN simulation of a gasifier. The simulated model will become more representative of the SCGP, and consequently more complex, in future design. By adding various process components, including an extensive syngas recycle stream, design keys will require adjustments to once again result in the desired amount of methanol product. However, the current ASPEN simulation allows for practical process selections and reasonable condition estimates for the beginning blocks of the multifaceted methanol process. The chosen processes will be fine-tuned in the future in order to optimize system performance and minimize its required investment and operating costs.

References

[1] C. Higman and M. van der Burgt, *Gasification*, Elsevier, Amsterdam, 2003.