PROCESS OF METHANOL PRODUCTION FROM BY-PRODUCT OFF-GAS GENERATED IN COKING OF MONGOLIAN COAL

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モンゴル産石炭のコークス化における副生ガスを原料としたメタノール製造プロセス

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A Mongolian coal was carbonized in laboratory to characterize the generated off-gas. Furthermore the readily available technologies for methanol production from coking off-gas were explored. Based on these results, appropriate process flow diagram in case of Mongolia was synthesized and computational simulation and rough cost estimation were carried out for this process. Consequently, this process was proposed for efficient utilization of Mongolian coal resources.

1. Introduction

Establishment of the country's first cokemaking plant has currently being discussed in Mongolia. However there is lack of study on possible way of utilization of by-products of cokemaking, namely the coke-oven gas (COG) and coal tar [1].

Conventionally the off-gas generated in coking plants has been used as fuel for heating applications or passes out to atmosphere after combustion causing waste of energy and air pollution [2]. Alternatively, due to high concentration of hydrogen and methane, the COG has being considered as suitable source for production of methanol [3]. Methanol has appeared to be not only highly demanded feedstock for chemical industry but also a promising alternative fuel for transport vehicles and gas turbine power generation [4].

In the current study a Mongolian coal was carbonized at laboratory scale. The generated off-gas was analyzed by gas chromatography (GC) to demonstrate its suitability for methanol synthesis. Furthermore, the available technologies for conversion of COG to methanol were explored, and an appropriate process flow diagram (PDF) was synthesized. The computational simulation of the process was carried out using commercial process simulator. The resulting dimensions of streams, units, and energy balance were used for cost estimation of the process.

2. Study of Mongolian coal

The two main bituminous coal mines play an important role in economics of the country - Tavan-Tolgoi (TT) and Naryn-Sukhait (NS). However NS coal has not been studied to satisfactory extends, and therefore it was selected for the case study.

The examination of available data of previous studies allow classifying NS coal to high volatile weakly coking coal that cannot be used for cokemaking by its own (Table 1). In coking blend NS coal might be used as high volatile supplementary component if the base coal with strong caking property is available, such as Mongolian TT coal.

Furthermore, Mongolian NS coal was carbonized at temperatures up-to 900^{0}C. The obtained off-gas was analyzed by GC. The carbonization apparatus consisted of electric furnace, fixed-bed reactor equipped with thermocouple and condensation system for removal of liquid and gaseous products (Fig.1). Table 2 shows the experimental conditions. The yield of coke was 67w% in average, the condensable liquid 18w% and off-gas 15w%. The off-gas was generally characterized by excess of hydrogen compared to carbon oxides, which was desirable for the methanol synthesis. It also contained considerable amount of methane which may become a source of syngas through reforming (Fig.2). Thus, the experiments have qualitatively proved that off-gas generated in carbonization of Mongolian NS coal could be suitable for synthesis of methanol.

3. Development of an appropriate process flow diagram for methanol production from coke-oven gas

It was assumed that the cokemaking plant will produce 1 million tons of coke per year. The amount of COG available for methanol synthesis would be approximately 259,875,000 cubic meters per year [5].

Various processes for each technological section of COG-to-MEOH plant were studied comparatively. The appropriate processes were selected according to following priorities: technological simplicity, low consumption of chemicals, less pollutants and low cost. Selection of deep desulfurization process within the methanol plant was closely affected by the selection of bulk desulfurization process in the by-product recovery cokemaking plant. Therefore relatively extended focus was paid on COG purification processes. For bulk desulfurization, the conventional absorption/stripping process was selected due to lower consumption of chemicals and less pollutant. Rectisol was selected for the deep desulfurization due to reliability and independence from consumable chemicals although it has higher investment and energy requirements. The tubular steam reformer was preferred to the autothermal reformer as it does not require expensive air separation unit (ASU) for pure oxygen. For methanol synthesis, low-pressure and low-temperature (LPLT) quench reactor was chosen due to easier operation and lower cost compared to LPLT tubular reactor, and the readiness for commercial application compared to the liquid phase reactor. For purification of raw methanol, the two-column distillation was preferred to single or multi-column distillation as those may either result in in-sufficient purity of methanol or higher cost and energy consumption. The literature indicates availability of gas turbines (GT) that can operate on low calorific purge gas from methanol synthesis after minor modification. Heat of GT exit gas as well as other excess process heat streams with temperatures higher than 300^0C was assumed to be converted to electricity using steam turbine with 33% efficiency. The comparative technological study has revealed that methanol can be produced from COG using readily available and reliable processes.

The appropriate process flow diagram of the plant was developed based on these selected processes (Fig.3) and then simulated using a commercial process simulator ChemCAD III (Fig.4). The simulation has resulted in annual production of 104,500 tons methanol, 206,716 MWh electricity and 125,600 MWh heat for district heating. The methanol conversion efficiency of the plant was estimated at 43.4% and the total efficiency at 78.2%. The methanol conversion efficiency might be increased by improving water removal unit after SMR and increasing recycle ratio in the synthesis loop.

Several options were compared for further improvement of the process. A combination of coal firing coke ovens and coal gasification unit [2] with the hot raw COG cracking and hot gas cleaning [8] has appeared as the promising way to improve the production process, although it faces some technical difficulties to be overcome in the future. The dehydration of methanol into DME may also be considered as a possible improvement of the process since DME could be blended with LPG and thus increase the marketability of the products. Once the methanol production plant will be installed, the DME producing facility can be installed with small additional equipment cost of approximately 10% of that of the methanol producing facility [9].

4. Cost estimation for methanol production from coke-oven gas

The results of computational simulation were used for cost estimations. The capital cost of the plant was estimated at 166 MUSD2010 using scaling factor and installation factors available in literature. An installed cost method was used for estimation of production cost [6]. The sensitivity analysis has shown that methanol might be produced at cost of 62-213 USD/t or at 138 USD/t in the base case. Compared to the current price of methanol in Asian market at 310-350 USD/t [7], the obtained values allow concluding that production of methanol from COG with the selected process flow diagram could be economically feasible.

5. Conclusion

According to the results of this study, combination of cokemaking plant and synthetic methanol plant within the same production boundary has appeared feasible both technically and economically. Moreover it might contribute to reduction of country's total dependence on imported transport fuel and to the development of chemical process industry in Mongolia.

References

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Table 1: Comparison of coking property of NS coal with typical coking coal

Parameters	Typ. coking coal	NS coal
Volatile matter, dmmf	19-35%	31-37%
Reflectance of Vitrinite	1.2-1.3%	0.5-0.84%
FSI		
weakly caking coal	3	1-6
moderately caking coal	4-5	
strongly caking coal	6-7	
RI	>45	60-75
Sapozhnikov thickness of plastic layer	14-17mm	7-11mm
Maximum fluidity	200-1000ddpm	14ddpm
Fe_2O_3 in ash	<10%	7.8-11.8%
CaO in ash	<3%	6.4-12.7 %
CSR (predicted)	>80	53-68
NKK window model	-	III

Table 2: Experimental conditions

Coal sample	Mongolian coal
Mass of coal sample	~65 g
Carbonization temperature	ambient ~ 900 °C
Carbonization atmosphere	nitrogen

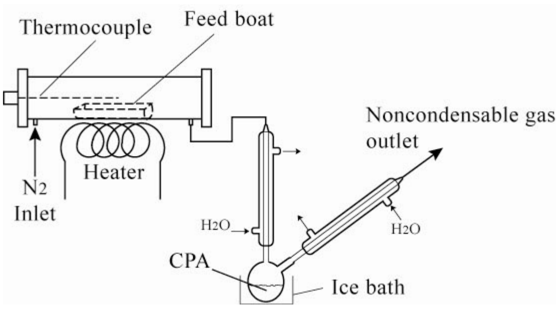

Fig.1: Schematic diagram of carbonization apparatus

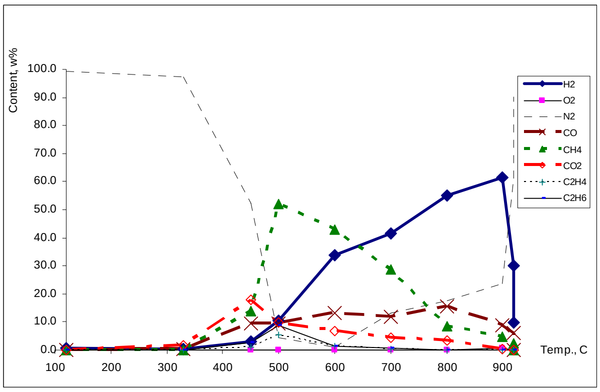

Fig.2: Change of off-gas composition from Mongolian NS coal at various temperatures of carbonization

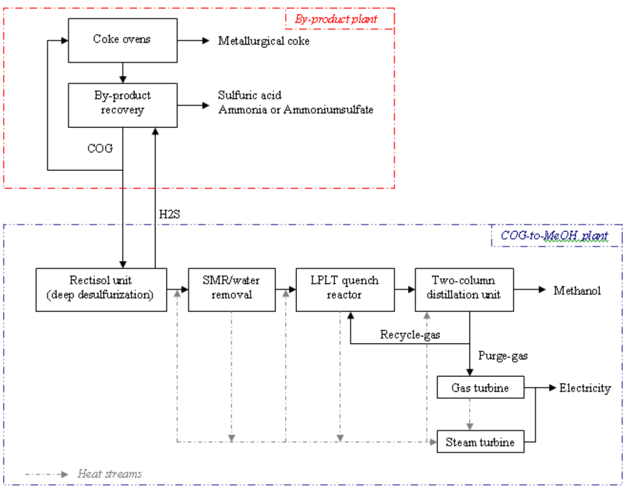

Fig.3: Process flow diagram for COG-to-Methanol plant

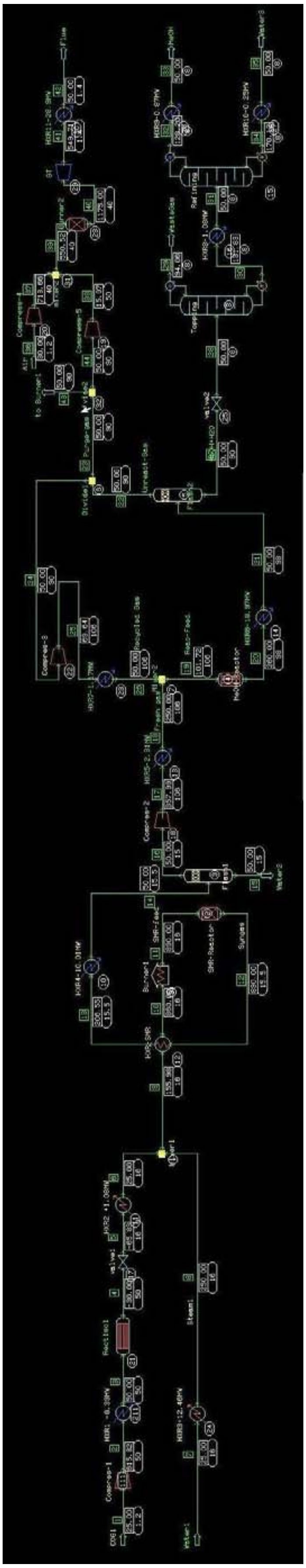

Fig.4: Process Flow Diagram of the COG-to-MeOH plant (Synthesized using ChemCAD III)