Process Design and Analysis of Coal-based Methanol to Aromatics Integrated with Light Hydrocarbons Conversion

Jianrong Jiang[a], Xiao Feng[a], Minbo Yang[a,*], Yufei Wang[b]

[a]Shaanxi Key Laboratory of Energy Chemical Process Intensification, School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China
[b]State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, 102249, China
 yangmb@xjtu.edu.cn

Methanol to aromatics is gradually becoming mature with years of research and development, which provides possibility for industrialization of coal to aromatics. However, methanol aromatization results in a quite low aromatics yield of about 40 % on the dry basis. In addition to aromatics, considerable light hydrocarbons are produced in methanol aromatization. Focusing on these light hydrocarbons, this paper proposes a novel process design that integrates coal to aromatics with steam reforming of light hydrocarbons in order to increase the yield of aromatics. First, a simulation model for producing aromatics from coal via methanol is developed and the mass and energy balances are obtained through rigorous simulation. Next, light hydrocarbon byproducts are considered to produce hydrogen-rich syngas via steam reforming, which is used as raw material to the methanol synthesis unit with syngas from coal gasification. Based on this idea, a novel process design where coal to aromatics is integrated with light hydrocarbons conversion is proposed. Such a novel design not only reduces the load of the water gas shift unit, but also simplifies the product separation unit. Based on rigorous simulation, the two processes are analysed in terms of mass balance, energy consumption, and economy. The results show that the aromatics yield of the integrated process increases by 146 %, the mass flow of products increases by 3.9 %, while CO_2 emission of the acid gas removal unit decreases by 12 %. Besides, the integrated process results in 87 % higher net present value than that of the non-integrated process.

1. Introduction

Aromatics are important petroleum derivatives that are widely used in synthetic fibre, synthetic rubber and synthetic resin. Conventionally, aromatics are mainly derived from petroleum. Most of the aromatics are produced from catalytic reforming and catalytic cracking units in refineries. With the increasing demand for aromatics, the production of aromatics from petroleum becomes unable to meet the demand in recent years. Aromatics from other sources attract more and more attention.

Producing aromatics from coal via methanol is a promising pathway, where coal is gasified to produce methanol that is then converted to aromatics by methanol aromatization. The process of methanol producing from coal gasification has been quite mature, while how to improve yields of aromatics from methanol is an active research area. Many recent publications aim to improve the selectivity of aromatics regarding catalysts and reactors. A highly shape-selective Mg-Zn-Si-HZSM-5 catalyst was developed by Li et al. (2016). It can result in over 98.9 % para-selectivity of xylene and 20.1 – 21.2 % p-xylene yield in 12 h of methanol to aromatics reaction. Jia et al. (2017) investigated nanometer HZSM-5 catalysts modified by ZnSiF6·6H₂O for producing aromatics from methanol, which had the highest selectivity to benzene, toluene and xylene (BTX) of about 51.3 % and the longest catalytic lifetime of about 234 hours. Zhang et al. (2017) developed an HZM-5 catalyst modified by cadmium, the aromatics selectivity of which was up to 63 wt%. As for reactors, Wang et al. (2014) proposed a two-stage fluidized reactor (TSFB) for aromatics production from methanol, and its carbon-based selectivity of aromatics reached 54.5 %. Two kinds of temperature-shifting three-stage fluidized bed reactor technologies were developed for the consecutive conversion of methanol and its intermediate products into aromatics, the aromatics selectivity of which were up to 66 % (Chen et al., 2019a) and 68 % (Chen et al.,

2019b). Although the aromatics selectivity of methanol to aromatics has been improved by these contributions, there are still notable light hydrocarbons produced in the process.

In order to improve this situation, a novel process of coal to aromatics integrated with light hydrocarbon reforming is proposed, which converts all light hydrocarbons into syngas to improve the process yield of aromatics. Firstly, the process of producing aromatics from coal via methanol is established in Aspen HYSYS. On this basis, a simulation model of coal to aromatics integrated with light hydrocarbon reforming is built. The mass and energy balances are then obtained according to the rigorous simulation. Next, mass balance, energy consumption and techno-economic analyses of the two processes are conducted and compared.

2. Process description

The block diagram of coal to aromatics (non-integrated) is shown in Figure 1a. Coal, oxygen and water are sent to the gasification unit to produce syngas. The syngas is then split into two streams, one of which is fed into the water gas shift unit to convert excess CO into hydrogen. After the two streams are combined, CO_2 and H_2S of the syngas are removed in the acid gas removal unit. The deacidified syngas is compressed and introduced into the methanol synthesis unit. Next, the synthesized methanol is dehydrated and fed to the methanol aromatization unit. Finally, the products of aromatization are separated in the separation unit to obtain the final products. However, the process produces a lot of light hydrocarbons besides aromatics. On the basis of Figure 1a, Figure 1b shows the process of coal to aromatics integrated light hydrocarbon reforming (integrated). Light hydrocarbon pretreatment unit and methane steam reforming unit are considered in the process to convert light hydrocarbons into syngas which is sent to methanol synthesis unit. It is noteworthy that all the light hydrocarbons below C_5 are sent into the light hydrocarbon pretreatment unit without separation, so the sequence of columns for light hydrocarbon separation is omitted from the product separation unit.
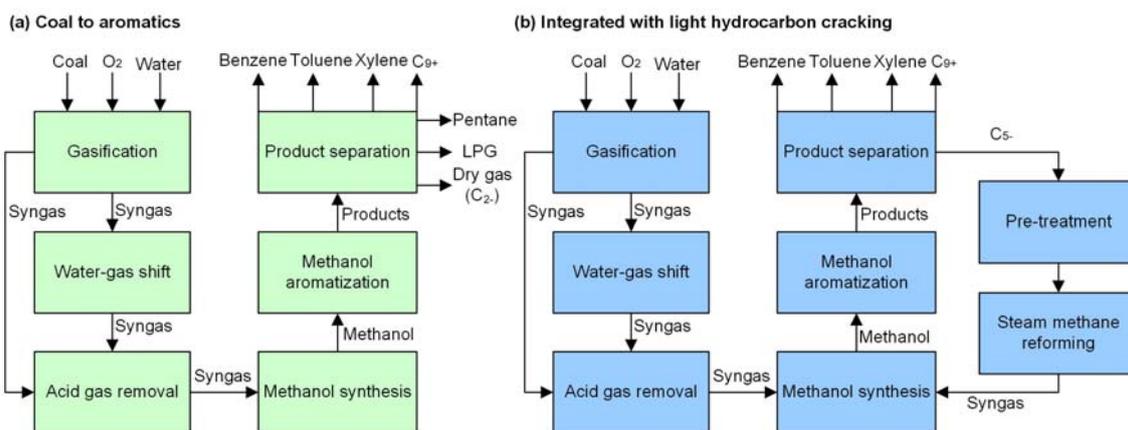
Figure 1: Block flow diagrams of two processes for producing aromatics from coal

3. Process modelling and simulation results

Both the two processes described in the previous section are modeled in Aspen HYSYS V10. Sour SRK is adopted as the property method for acid gas removal unit because it is suitable for acid gas removal system (Aspen HYSYS, 2017), while Peng-Robinson is employed for the other units. For the non-integrated process, the coal gasification reactor refers to the improved Merrick's model (Zhou et al., 2018), where the pyrolysis and gasification parts are simulated by yield reactor and Gibbs reactor. Two-stage surfur-resistance shift is simulated by equilibrium reactor (Andreeva et al., 2002). The acid gas removal unit adopts single-stage Rectisol wash to remove CO_2 and H_2S simultaneously (Shangguan et al., 2012). The methanol synthesis process consists of two parts: methanol synthesis and methanol purification, which are simulated by plug flow reactor and distillation columns (Luyben, 2010). The model of methanol aromatization unit is established according to fluidized bed technology (Wang et al., 2014). The product separation unit consists of aromatics and non-aromatics separation, light hydrocarbon recovery and BTX recovery, which are simulated referring to reference (Zhang et al., 2019). As for the integrated process, both the light hydrocarbon pretreatment unit and steam reforming unit refer to reference (Yang and You, 2018). Conversion reactor and plug flow reactor are used to simulate the pretreatment reactor and steam reforming reactor. The product separation unit consists of aromatics and non-aromatics separation and BTX recovery.

In this study, both the two processes consume 852,571 kg/h of coal. The operating time is 8,000 h/y. As shown in Table 1, for the non-integrated process, aromatics only accounts for 40.6 wt% of the total products. Specifically, desired BTX products take up 30.4 wt% of the total. The aromatization of methanol produces considerable light hydrocarbons. Liquefied petroleum gas (LPG) accounts for the largest proportion, about 41.2 wt%. Dry gas is another notable product that occupies 10.1 wt%, while C_5 mixture is about 8.1 wt%. The main components of dry gas are C_2 and lighter components. As for the integrated process, all the products are aromatics because light hydrocarbons are converted to syngas. BTX take up 85.3 wt% of the total products. Xylene is the largest contributor accounting for 52 wt% of the total products. Toluene and benzene occupy 25.4 wt% and 8 wt%. In comparison, the aromatics yield of the integrated process increases by 146 %. The total mass flow of products in the integrated process is 3.9 % higher than that in the non-integrated process. In addition, the integrated process reduces the CO_2 emission of the acid gas removal unit by 12 % compared with the non-integrated process. This is because the hydrogen-rich syngas generated by reforming of light hydrocarbons can improve the ratio of carbon to hydrogen of coal-based syngas, which reduces the proportion of coal-based syngas entering the water gas shift unit.

Table 1: Mass and energy balances for two processes of producing aromatics from coal

	Non-integrated	Integrated
Input		
Coal (kg/h)	852,571	852,571
O_2 (kg/h)	667,343	667,343
Water (kg/h)	95,462	80,795
Stripping N_2 (kg/h)	5,248	5,248
Makeup Methanol (kg/h)	2,848	2,759
Output		
Benzene (kg/h)	9,951	25,487
Toluene (kg/h)	31,708	81,212
Xylene (kg/h)	65,002	166,488
C_{9+} (kg/h)	18,336	46,964
Pentane (kg/h)	24,973	-
LPG (kg/h)	126,935	-
Dry gas (kg/h)	31,223	-
Direct emissions		
Ash (kg/h)	127,886	127,886
H_2S (kg/h)	6,517	6,517
CO_2 (kg/h)	1,127,297	991,578
Utilities		
Power (MW)	70.49	82.59
Fired Heat (MW)	-	1,736.14
LP Steam (MW)	429.91	919.75
Cooling Water (MW)	1,549.68	1,905.57
Refrigerant 1 (-25 °C, MW)	58.36	18.67
Refrigerant 3 (-65 °C, MW)	154.87	43.68
HP Steam Generation (MW)	724.47	606.33
MP Steam Generation (MW)	368.65	959.35

As for the utility consumed in the two processes, the integrated process needs a large amount of fired heat to support light hydrocarbon reforming reaction. However, due to the simplified product separation unit, the integrated process saves a considerable amount of cold utility. Its Refrigerant (1) and Refrigerant (3) are only 32 % and 28.2 % of those consumed in the non-integrated process. The generated medium pressure steam (MP Steam Generation) of the integrated process is 160 % higher than that of the non-integrated process, as syngas generated by light hydrocarbon reforming is fed to the methanol synthesis reactor, which enlarges the methanol synthesis reactor to 2.56 times that of the non-integrated process.

4. Techno-economic analysis

4.1 Capital investment

In general, the total capital investment consists of bare-module investment, site preparation cost, contingencies and contractor's fee, land cost, royalties cost, plant startup cost, and working capital. In this study, Aspen Process Economic Analyzer V10 is employed to estimate the equipment purchase cost.

The total investment cost of the two processes is calculated according to the reference (Seider et al., 2009), as shown in Figure 2a. The total bare module cost is the largest contributor by 56.2 % of the total capital investment in the non-integrated process. The working capital takes 13.1 % of the total, and the contingencies and contractor's fee are also a major contributor, about 11.6 %. Similar to the non-integrated process, the total bare module cost is also the most dominated part of the investment cost of the integrated process, followed by working capital and contingencies and contractor's fee.

The capital investment of the integrated process is 1.71 times as much as the non-integrated process. The simplified product separation unit in the integrated process reduces the capital investment, but the influences of added light hydrocarbon reforming unit, enlarged methanol synthesis unit, and the distillation sequence for aromatics separation are more significant. As a result, the capital investment of the integrated process is higher than that of the non-integrated process.

4.2 Annual sales revenue

The annual sales revenues of the integrated and non-integrated processes are obtained by summing sales of all products and presented in Figure 2b. The prices of products come from the Chinese market price in 2019.

The annual sales revenue of the non-integrated process is $ 1,847.2 M. Xylene is the largest contributor for the annual sales revenue by 30.2 %. LPG is the second, accounting for 26.7 % of the total sales. BTX take up 47.7 % of the total sales, and toluene accounts for 13.7 %. As for the integrated process, the total annual sales revenue is $ 2,546.7 M. Xylene contributes to the largest proportion of the annual sales revenue by 56 %. BTX occupy 88.4 % of the total sales, and toluene takes up 28.9 %.

The annual sales revenue of the integrated process is significantly higher than the non-integrated process. The aromatics yield of the non-integrated process is only 40.6 %. The prices of other products, such as LPG, pentane and dry gas, are much lower than that of aromatics. While the integrated process converts these products into aromatics, increasing the process aromatics yield by 146 %. The hydrogen-rich syngas produced by light hydrocarbon reforming improves the ratio of carbon to hydrogen of coal-based syngas, increasing the mass flow of products by 3.9 %.

4.3 Annual production cost

The annual production costs of the integrated and non-integrated processes are calculated according to the reference (Seider et al., 2009), as shown in Figure 2c. The feedstock cost accounts for the largest proportion in the non-integrated process, about 39.2 %. The second contributor is the utility cost, accounting for 25.1 % of the total. Besides, general expenses are another major contributor, taking up 15.6 %. As for the integrated process, the largest contributor is utility cost, about 31.2 %, followed by the feedstock cost, accounting for 28.7 %.

The total production cost of the integrated process is 1.38 times as much as that of the non-integrated process. The main reason is that a large amount of fuel is consumed to support light hydrocarbon reforming reaction in the integrated process, which results in a much higher utility cost, about 1.69 times of the non-integrated process. The general expenses of non-integrated process are higher due to higher annual sales revenue. The investment cost of integrated process is 1.71 times as much as the non-integrated process, which results in higher depreciation cost and maintenance cost.
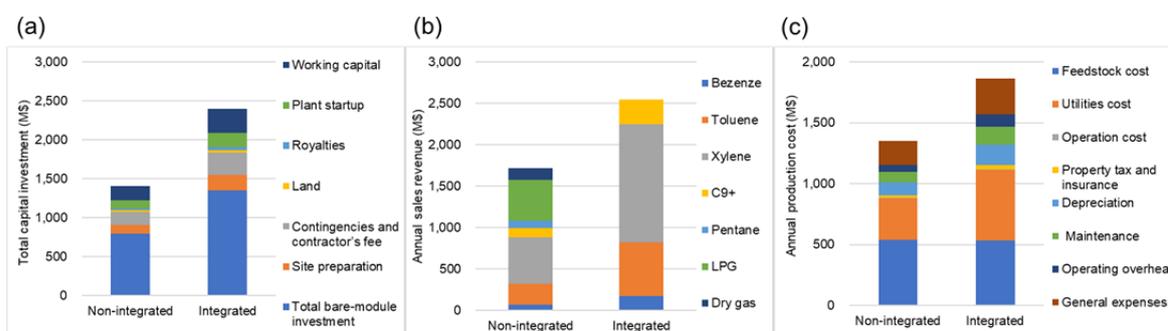
Figure 2: Comparisons of the two processes for producing aromatics from coal: (a) Total capital investment, (b) Annual sales revenue, and (c) Annual production cost.

4.4 Net present value

The net present value (*NPV*) is one of the principal profitability measures that consider the time value of money in terms of discounted cash flows. The cash flow of the project in the whole life cycle should be previously calculated before estimating the net present value, as shown in Eq(1).

$$CF_t = (1 - tax)(S - C) + D \qquad (1)$$

where CF_t is the cash flow in year t, tax is the tax rate, S is the annual sales revenue, C is the production cost, and D is the depreciation.

After calculating the cash flow in each year of the project life, the net present values for producing aromatics from methanol and naphtha can be obtained by Eq(2), where i is the interest rate.

$$NPV = \sum_{t=0}^{n} CF_t (1 + i)^{-t} \qquad (2)$$

Figure 3 shows the cumulative present value for non-integrated and integrated processes.
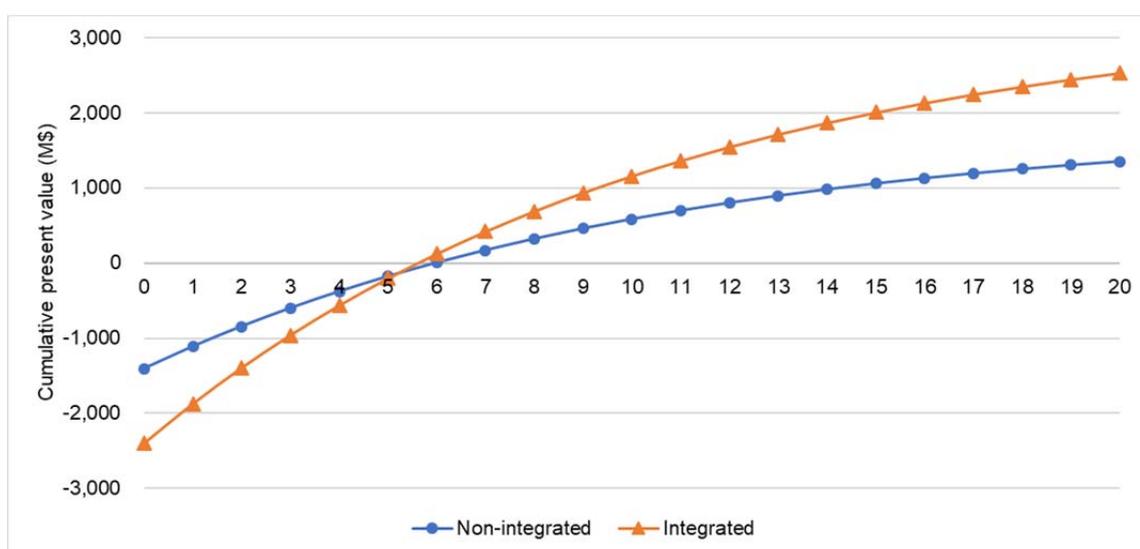
Figure 3: Cumulative present value of two processes of producing aromatics from coal

It can be seen that the curve of non-integrated process starts from a higher point due to the lower total capital investment. However, the net present value of the integrated process increases more rapidly. The cumulative present value of the integrated process exceeds the non-integrated process in the 6 years. The cumulative present value of non-integrated process and integrated process finally reach \$ 1,352 M and \$ 2,529 M. Such a result indicates that the integrated processes are more economically attractive than the non-integrated process.

5. Conclusions

Based on the process for producing aromatics from coal via methanol, a novel process of producing aromatics from coal-based methanol integrated light hydrocarbon reforming was proposed in this study. The unique feature of the proposed process was that the light hydrocarbons produced in methanol aromatization were converted into aromatics through a series of reactions including steam reforming, methanol synthesis and methanol aromatization, which increased the yield of aromatics by 146 %. The CO_2 emission of acid gas removal unit decreased by 12 %, while the total mass flow of products increased by 3.9 %. The integrated process consumed large amounts of fired heat due to the additional light hydrocarbon reforming device. However, its consumption of Refrigerant 1 and Refrigerant 3 was only 32 % and 28.2 % of the non-integrated process because of the simplified product separation unit. The techno-economic analysis showed that the total capital investment, annual sales revenue and annual production cost of the integrated process were higher the non-integrated process. The cumulative present value of the integrated process was 1.87 times of the non-integrated process. The result indicated that the integrated process is more attractive for aromatics production.

In addition to the conversion of light hydrocarbons via methanol, the direct aromatization of C_{3+} is also an alternative. More alternative technologies will be considered in the future works to find the most effective process for aromatics production.

Acknowledgements

References

Andreeva D., Idakiev V., Tabakova T., Ilieva L., Falaras P., Bourlinos A., Travlos A., 2002, Low-temperature water-gas shift reaction over Au/CeO$_2$ catalysts, Catalysis Today, 72(1), 51-57.

Aspen HYSYS V10, 2017, Help System, HYSYS Property Environment, Aspen Inc.

Chen Z., Hou Y., Song W., Cai D., Yang Y., Cui Y., Qian W., 2019a, High-yield production of aromatics from methanol using a temperature-shifting multi-stage fluidized bed reactor technology, Chemical Engineering Journal, 371, 639-646.

Chen Z., Hou Y., Yang Y., Cai D., Song W., Wang N., Qian W., 2019b, A multi-stage fluidized bed strategy for the enhanced conversion of methanol into aromatics, Chemical Engineering Science, 204, 1-8.

Jia Y., Wang J., Zhang K., Liu S., Chen G., Yang Y., Ding C., Liu P., 2017, Catalytic conversion of methanol to aromatics over nano-sized HZSM-5 zeolite modified by ZnSiF6•6H$_2$O, Catalysis Science & Technology, 7(8), 1776-1791.

Li J., Tong K., Xi Z., Yuan Y., Hu Z., Zhu Z., 2016, Highly-efficient conversion of methanol to p-xylene over shape-selective Mg–Zn–Si-HZSM-5 catalyst with fine modification of pore-opening and acidic properties, Catalysis Science & Technology, 6(13), 4802-4813.

Luyben W.L., 2010, Design and control of a methanol reactor/column process, Industrial & Engineering Chemistry Research, 49(13), 6150-6163.

Seider W.D., Seader J.D., Lewin D.R., Widagdo S., 2009, Product and process design principles, John Wiley & Sons, Hoboken, America.

Shangguan J., Chang L., Miao M., 2012, Gas purification and separation technologies, Chemical Industry Press, Beijing, China.

Wang T., Tang X., Huang X., Qian W., Cui Y., Hui X., Yang W., Wei F., 2014, Conversion of methanol to aromatics in fluidized bed reactor, Catalysis Today, 233, 8-13.

Yang M., You F., 2018, Modular methanol manufacturing from shale gas: Techno-economic and environmental analyses of conventional large-scale production versus small-scale distributed, modular processing, AIChE Journal, 64(2), 495-510.

Zhang D., Yang M., Feng X., 2019, Aromatics production from methanol and pentane: Conceptual process design, comparative energy and techno-economic analysis, Computers & Chemical Engineering, 126, 178-188.

Zhang Y., Qu Y., Wang D., Zeng X.C., Wang J., 2017, Cadmium modified hzsm-5: a highly efficient catalyst for selective transformation of methanol to aromatics, Industrial & Engineering Chemistry Research, 56(44), 12508-12519.

Zhou H., Xie T., You F., 2018, On-line simulation and optimization of a commercial-scale shell entrained-flow gasifier using a novel dynamic reduced order model, Energy, 149, 516-534.