

A Novel Design of Methyl Methacrylate Synthesis Process with Low CO₂ Emission

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Methyl methacrylate (MMA) is an important raw material for synthesising polymethyl methacrylate, plastic modifier, and surface coating. In this paper, an optimum “energy saving and low emission” process is proposed for MMA production. MMA is synthesised from ethylene and synthetic gas generated from coal chemical looping gasification (CLG), which can largely reduce CO₂ emission. Firstly, the reaction mechanism of coal CLG is investigated using molecular dynamics simulation. Secondly, to verify the feasibility of the process, the steady-state simulation of MMA production process is carried out by Aspen Plus. Finally, based on the steady-state simulation results, one control scheme is verified with Aspen Dynamics to strictly control the purity of MMA.

1. Introduction

Methyl methacrylate (MMA) is widely used in synthesising polymethyl methacrylate, plastic modifier, and surface coating (Sergeev et al., 2020). MMA can be synthesised through synthesis gas or other materials through several methods, such as acetylcholine (ACH) method (Abe et al., 1999), isobutylene oxidation method, and ethylene method. ACH method was developed and industrialised by ICI in 1937, and is still in a monopoly position up to now. However, scholars have tried to find an alternative process of ACH method to produce MMA due to its deficiencies like extremely poisonous raw materials and unenvironmentally friendly production process. The application of Isobutylene oxidation method is hindered seriously by its high cost of raw material. Comparatively, ethylene method has gradually attracted people's attention because of its short process and environmental friendliness as a post-process of coal chemical industry (Schwendeman et al., 2004). Synthesis gas is an essential material in ethylene method, which can be obtained by various methods. Particularly, coal chemical looping gasification (CCLG) as an effective way to produce synthesis gas and reduce emission of CO₂, has a promising application prospect in the coal chemical industry field. During a process exploration, it is necessary to study and discuss the reaction mechanism using molecular dynamic (MD) simulation method. As a popular MD simulator, ReaxFF was proposed by van Duin et al., (2001) and designed to remedy the defect between quantum chemical and empirical force field by computational chemical methods. In practice, it is hard to calculate systems that include more than 100 atoms in quantum chemical. However, ReaxFF has capability of simulating the physical and chemical process of a system containing millions of atoms with the time scale reaching 100 ns (Islam et al., 2015). Based on above motivations, a methacrylate synthesis process of coal-syngas-MMA is proposed, which combines CCLG process and dry methane reforming (DMR) reaction to reduce CO₂ emission. The feasibility of the process is verified by multi-scale simulation. Firstly, the influence of reaction temperature on the product distribution of CCLG process is studied by using Reactive Force Field reaction molecular dynamics (ReaxFF-RMD) method. The steady-state and dynamic simulation of the process are carried out using Aspen Plus and Aspen Dynamics software.

2. Molecular dynamic simulation process and results analysis

The first step of molecular dynamic simulation is to establish CLG system models using Materials Studio (MS) 7.0 software, including the molecular model of Fe₂O₃, char, and CO₂.

The oxygen carrier Fe_2O_3 , which provides lattice oxygen to react with carbon and steam, is an important catalyst in CLG. Fe_2O_3 is an ionic crystal belonging to the R-3C space group, with cell parameters of $a = b = 5.035 \text{ \AA}$, $c = 13.72 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ (Yanagihara et al., 2006). According to these parameters, a Fe_2O_3 lattice is initially built in Figure 1, in which Figure 1a and Figure 1b are top and side view of Fe_2O_3 lattice respectively. Then an optimised geometry structure is constructed using Forcite module, taking the minimum energy of the structure as the optimisation object.

The annealing simulation of 600 ps is conducted to ensure that the minimum value of energy is obtained on the whole potential energy surface. The anneal simulation chooses Nose as temperature control method based on canonical ensemble (NVT) system. The temperature is increased from $26.85 \text{ }^\circ\text{C}$ to $326.85 \text{ }^\circ\text{C}$, and then is decreased to $26.85 \text{ }^\circ\text{C}$ at $6 \text{ }^\circ\text{C/ps}$ speed in 6 times cycling. The minimum energy structure obtained from the results of annealing is chosen as the input structure of cube box.

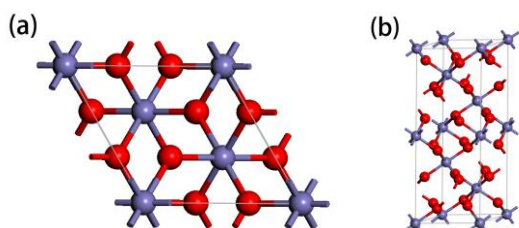


Figure 1: Initial Structure of Fe_2O_3 model

The char models proposed by Fidel Castro Marcano (2012) were modified by Perl model for coal modeling to facilitate the evaluation of its chemical and physical properties. The initial structures of char models are shown in Figure 2, in which Figure 2a, Figure 2b, and Figure 2c are char structure models of $\text{C}_{19}\text{H}_{30}\text{O}$, $\text{C}_{20}\text{H}_{30}\text{O}$, and $\text{C}_{52}\text{H}_{28}\text{O}_2$. The processes of optimising geometry structure and annealing simulation are the same as Fe_2O_3 .

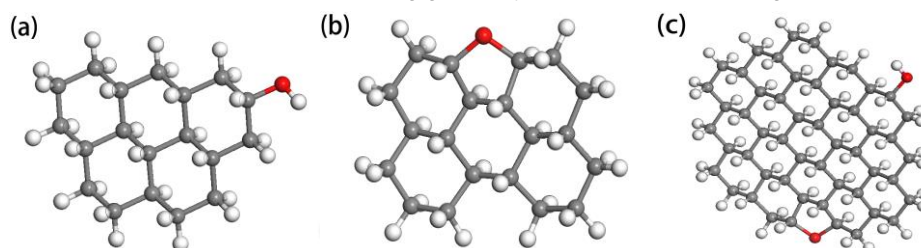


Figure 2: Initial structures of Char model

Based on a mass ratio of char: Fe_2O_3 in 4:6, the Fe_2O_3 , char, and CO_2 models are input into a $30 \times 30 \times 30 \text{ \AA}$ cube box. Then the geometry optimisation and annealing are performed again to stabilise the energy of whole system. The final structure of Fe_2O_3 -char- CO_2 system is shown in Figure 3.

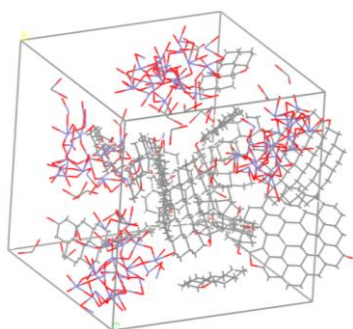


Figure 3: Final structure of Fe_2O_3 -char- CO_2 system in $30 \times 30 \times 30 \text{ \AA}$ cube box

ReaxFF-RMD simulation is carried out using reax/C module in LAMMPS software package. The specific parameters during molecular dynamics are as follows: initial temperature is $26.85 \text{ }^\circ\text{C}$, final temperature is $1,826.15 \text{ }^\circ\text{C}$, heating speed is $7 \text{ }^\circ\text{C/ps}$, step size is 0.25 fs , total simulation steps are $1,200,000$, and total

simulation time is 300 ps. The whole process is built based on NVT system. After ReaxFF-RMD, the trajectory and bond order results data are further analysed. The bond cutoff coefficient is set as 3.0.

The relationship between temperature and the number of pieces at 300 °C to 1,500 °C is shown in Figure 4. At the initial stage of reaction (300 °C to 600 °C), the number of hydrogen fragments are steadily increasing due to the break of C-H bond in char molecular. At the same time, the number of CO₂ fragments are decreasing and tends to be stable when the temperature reaches 750 °C. The number of CO fragments are fairly stable at the beginning when the temperature is below 600 °C. However, it starts to rise significantly when the temperature reaches 600 °C. There is no significant change in the number of hydrocarbons. It can then make a conclusion that the ideal reaction condition can be obtained by controlling the reaction temperature at 750 °C - 850 °C, and the continuously increasing temperature has small effect on the reaction.

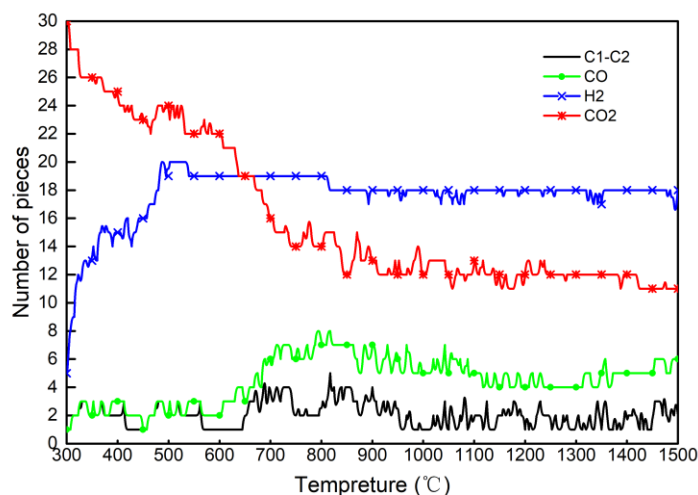


Figure 4: The relationship between the number of pieces and the simulated temperature

3. Coal-syngas-MMA process simulation

To verify the feasibility of the process, the schematic diagram of coal-syngas-MMA process is shown in Figure 5, in which the block marked by (1), (2), and (3) represent CLG-DMR, Rectisol, and GAS-MMA processes respectively. Char, the pyrolysed product of coal, is selected as the raw material of coal-syngas-MMA process. Char is unable to directly define in Aspen plus software because it contains variety of complex structures and elements. In order to describe its composition and physical properties properly, char is defined as unconventional components according to the results of proximate and element analysis (Chelgani et al., 2008).

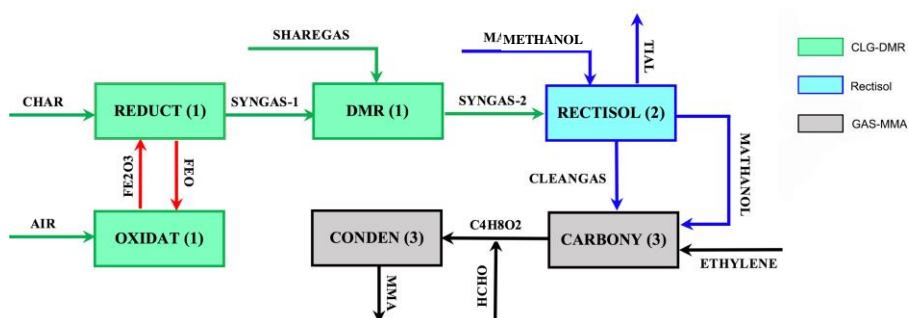


Figure 5: Schematic drawing of coal-gas-MMA process

At first, some modifications have been applied to the traditional CLG process to reduce CO₂ emission, which is shown in Figure 6. Various elements in char are defined through FORTRAN language in DECOMPOS (Zhang et al., 2019). After decomposition, char is mixed with oxygen carrier in the mixer module. Based on the results in ReaxFF-RMD, the reduction reaction is established in the REDUCT model using Rgibbs module in steam environment. After the separation of Fe₂O₃ and synthesis gas, the mixed stream of Fe₂O₃ and air (79 %

N_2 , 21 % O_2) are fed into OXIDAT. In the OXIDAT module, FeO is oxidised into Fe_2O_3 . To further reduce the content of CO_2 in crude synthesis gas, the crude synthesis gas is mixed with shale gas, and then delivered to DMR reactor in which methene is reacted with carbon dioxide. This reactor uses RPlug module. In this process, the CO_2 emission is largely reduced.

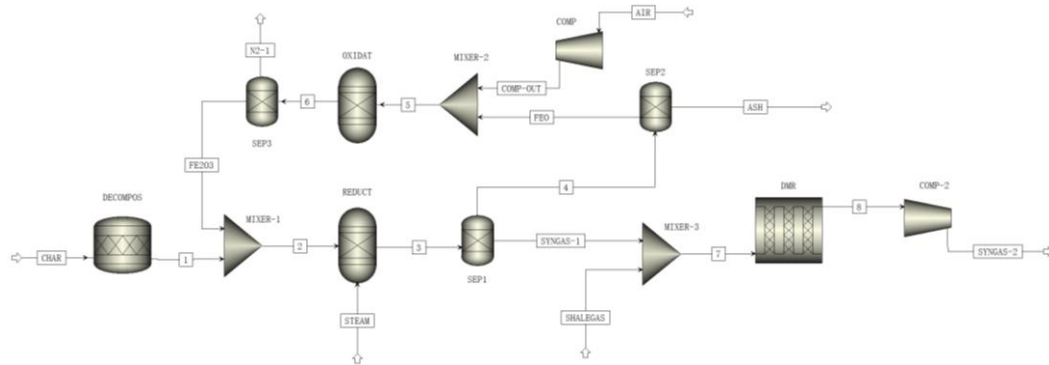


Figure 6: Simulation flowsheet of CLG-DMR process in Aspen Plus software

The simulation flowsheet of Rectisol process is then shown in Figure 7. In this part, crude synthesis gas is purified by Rectisol process. At the temperature of $-50\text{ }^{\circ}\text{C}$ and pressure of 3.3 MPa, impurities such as H_2S are absorbed by low-temperature methanol with a molecular ratio of 1:1. Cleaner synthesis gas and methanol are obtained at the top and bottom of the absorption tower.

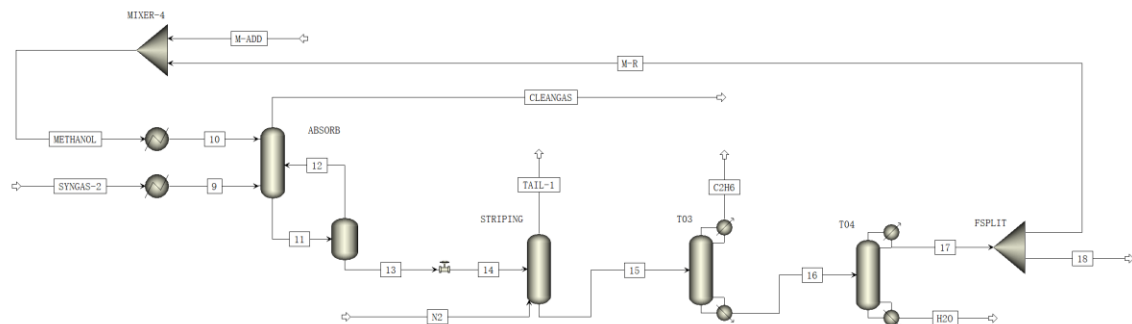


Figure 7: Simulation flowsheet of Rectisol process in Aspen Plus software

Finally, CO , ethylene, and methanol are mixed in MIXER-6 and delivered to CABONY to produce methyl propionate. Then methyl propionate in FLASH-2 bottom are purified by distillation. Owing to the quite close boiling point of each component, conventional distillation process would cause high energy consumption in separating this kind of mixture. So the extraction distillation is used in this work. Formaldehyde, the raw material in the following reaction section, is used as the extractant, which saves the energy for the recovery of extractant. The condensation reactions are set in CONDEN. The product of condensation reaction is separated by distillation, with 99.9 wt% MMA product is obtained from bottom. The simulation flowsheet is shown in Figure 8.

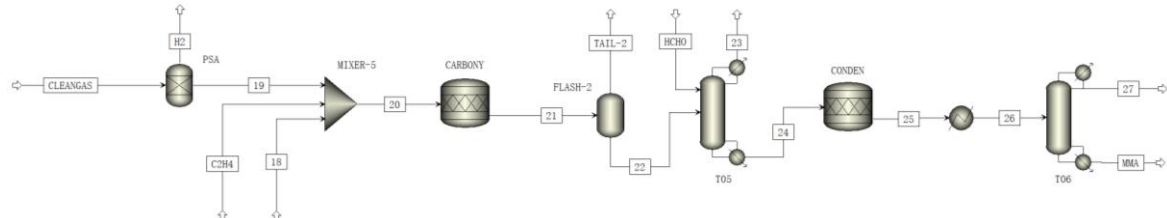


Figure 8: Simulation flowsheet of GAS-MMA process in Aspen Plus software

The simulation results of major streams are listed in Table 1. It can be seen that the mass flow and CO_2 molecular fraction of synthesis gas after CLG and DMG process are 552.3 kg/h and 0.6 %, and the mass

fraction of MMA in MMA stream is 99.9 %. Reducing pollution is an eternal topic for human beings (Gonzalez-Barriuso et al., 2019). The process largely reduces the emission of CO₂ and achieves the aim of pollution reduction. The effect of reactor temperature and T06 column parameters on the process is further analysed in the following section for safe operation purposes.

Table 1 simulation results of Coal-syngas-MMA process

Data Item	CHAR	SYNGAS-1	SHAREGAS	SYNGAS-2	CLEANGAS	MMA
Simulated Temperature (°C)	130	658.2	30	1,000	-50	173.5
Simulated Pressure (MPa)	0.1	2	0.2	0.2	3.3	0.6
Vapor Fraction	0	1	1	1	1	0
Mass Flow (kg/h)	200	498.2	54.1	552.3	481.1	1,235
N ₂	0	3	2.2	5.3	5.2	0
H ₂ O	0	50	0.1	50.1	0	0.002
H ₂	0	11.9	0	27.7	27.7	0
CO	0	229.3	0	448.7	446.9	0
CO ₂	0	174	2.1	3.7	0.3	0
CH ₄	0	24.9	38.9	1.0	0.9	0
C ₂ H ₆	0	0	5.6	5.6	0	0
C ₃ H ₈	0	0	4.4	4.4	0	0
H ₂ S	0	5	0.8	5.8	0	0
CHAR	200	0	0	0	0	0
MMA	0	0	0	0	0	1,235

4. Plant wide control

In order to mainly control the purity of MMA product, the process is simplified by steady-state simulation concerning reactor and distillation column only. Then, the simplified dynamic model of condensation reactor and the MMA distillation process is established by using Aspen Dynamics software as shown in Figure 9.

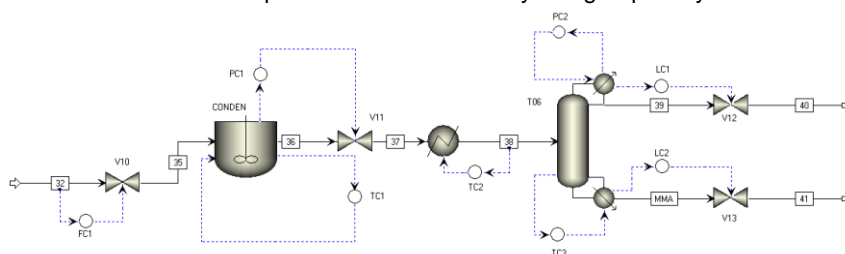


Figure 9: dynamic control scheme of condensation reaction and MMA distillation process

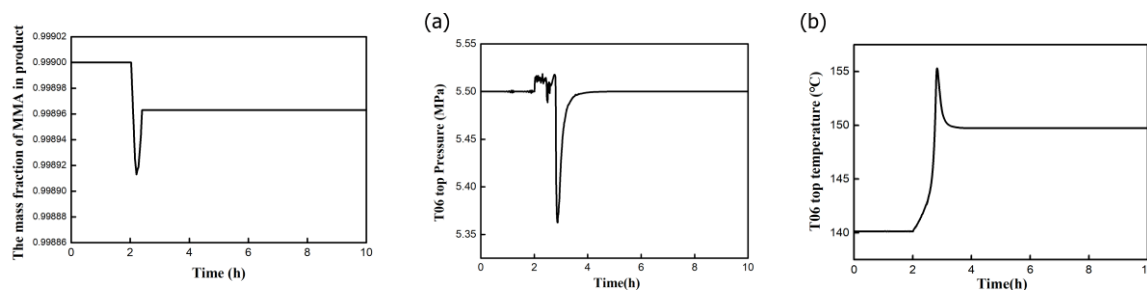


Figure 10: Effect of reactor temperature at 2 h on the mass fraction of MMA

Figure 11: Effect of reboiler temperature on T06

The mass fraction of MMA in product is analysed to ensure that the quality of product is stable. The temperature of the reactor is taken as an example to test the dynamic behavior of the mass fraction of MMA in

product under the action of the control system (Cui et al., 2019). The change of the mass fraction of MMA in product after reducing reactor temperature by 10 % at 2 h is shown in Figure 10. The mass fraction of MMA in MMA stream is decreased firstly and then increased to a stable value of 0.998963.

The change of the T06 top temperature after increasing reboiler temperature by 10 % at 2 h is depicted in Figure 11a, and the change of the T06 top pressure after increasing reboiler temperature by 10 % at 2 h is depicted in Figure 11b. The T06 top pressure fluctuates and then recovers back to the previous value. It can be seen that the T06 top temperature increases and then approaches a stable value of 150 °C, which proves the stability of the control scheme given in Figure 9.

5. Conclusions

This paper proposes a novel design of coal-syngas-MMA process which combines several emission reduction measures. First, the ReaxFF-RMD simulation is applied to find the appropriate temperature of reduction reaction in CLG process. Results from MD show that the ideal reaction condition can be obtained by controlling the reaction temperature from 750 °C to 850 °C. Second, the coal-syngas-MMA process is simulated using Aspen Plus software, with results showing that the mass flow and CO₂ mole fraction of synthesis gas after CLG and DMG process are 552.3 kg/h and 0.6 %, and the purity of MMA is 99.9 wt%. Finally, one control scheme is designed to control the purity of MMA product and verify the stability of distillation column of MMA by using Aspen Dynamics software. In the near future, considering the CLG reaction can be affected by several factors, the additional conditions such as pressure will be taken into consideration. To further improve the feasibility of the coal-syngas-MMA process, the work will also take various measures such as economical optimisation to optimise the process in general.

Acknowledgments

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