

The Orthogonal Test of the Methanol Synthesis from Biomass

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Abstract: In order to research reaction conditions to change the agricultural residues into the fuel methanol, pyrolysis test of cornstalk biomass fuel gas by the thermochemical method, and the optimum tests which the synthesis gas produced in cornstalk fuel gas were performed. When the kinds, particle size, the ways of stuffing and activation of catalyst, and syngas composition keep constant, the orthogonal test of methanol synthesis reaction factors (such as pressure and temperature of synthesis reaction, and entrance flow of syngas) were carried out in a tubular-flow integral and isothermal reactor. The influence order of three representative factors in the time space yield of CH₃OH is determined through orthogonal test. The order is arranged like this, entrance flow of syngas, reaction pressure and reaction temperature. The optimum combination of three factors is as follows, temperature 250°C, pressure 4 MPa, and entrance flow of syngas (standard condition) 0.6mol·h⁻¹.

Keywords: methanol; biomass; corn straw; catalyst; synthesis

1. INTRODUCTION

The reaction system of the methanol synthesis from CO, CO₂ and H₂ in biomass syngas belongs to the reaction system of gas phase and absorbing heat. The reaction pressure, temperature and entrance flow of syngas are all important factors which influence space time yield of methanol. In order to research the best combination of these three factors, we carried out the orthogonal test of the methanol synthesis.

2. THE ORTHOGONAL TEST OF THE METHANOL SYNTHESIS

2.1 Raw materials and main equipments for the test

Corn straw(which includes root, stalk, leaves), air-dry in nature, size is 2cm or 3cm ;

C301 Cu-based catalyst (Particle size is 0.246mm×0.175mm);

XFF-1000 down-flow fixed bed gasifier;

JA-five troughs tubular-flow integral and isothermal reactor.

2.2 Test process

The corn straw was used as feedstock , the biomass fuel gas was produced by the thermochemical method in XFF-1000 down-flow fixed bed gasifier. The compositions (mole fraction) of this fuel gas are CO 15.8%, CO₂ 12.5%, H₂ 12.6%, CH₄ 1.4%, O₂ 2.1%, C₂H₄ 0.5%, C₂H₆ 0.1%, C₂H₂ 0.03%, N₂ 55.0%, a little tar and sulfide. After processing the desulfurization, deoxy, catalytic cracking of tar, purification and hydrogenation, the

quality straw syngas was produced for methanol synthesis^[1]. The compositions (mole fraction) of this syngas are H₂ 40.27%, N₂ 37.73%, CO 11.54%, C_nH_n(=CH₄, C₂H₂, C₂H₄, C₂H₆) 1.14%, CO₂ 9.22%. The catalytic test of methanol synthesis for straw syngas over a domestic Cu-based catalyst C301 were carried out in JA-five troughs tubular-flow integral and isothermal reactor. Test conditions and processes are the same as reference^[2].

2.3 Design of the orthogonal test

The reaction temperature, pressure and entrance flow of syngas were considered as A,B and C, respectively. The scheme of the orthogonal test shows in Table 1.

Table 1 Factor level of orthogonal test

Test factors	Test level		
	1	2	3
Reaction temperature (°C)	240	250	260
Reaction pressure (MPa)	4	5	6
Entrance flow of syngas (standard condition) (mol/h)	0.3	0.6	0.9

2.4 Test results

We obtained the test data by the orthogonal test. The test results were obtained after processing the material balance of reaction system (see Table 2). The variance analysis of test results are shown in Table 3, 4, and 5, respectively.

3. CONCLUSIONS

The test and statistic analysis results show that the order which these three factors influence space time yield of methanol are entrance flow of syngas, reaction pressure and reaction temperature, orderly. The optimum combination

which made methanol time-space yield maximum is $A_2B_1C_2$, namely reaction temperature 250 °C, reaction pressure 4MPa and entrance flow of syngas $0.6\text{mol}\cdot\text{h}^{-1}$.

Table 2 Results and calculation of multi-factor orthogonal test for straw syngas

test No.	factors			indexes		
	Reaction temperature	Reaction pressure	Entrance flow of syngas	CO conversion (%)	CO ₂ conversion (%)	CH ₃ OH time-space yield ($10^{-2}\text{kg/kgcat}\cdot\text{h}$)
1	1	1	1	21.43	0.23	5.01
2	1	2	2	16.61	0.45	7.96
3	1	3	3	20.17	0.76	13.65
4	2	1	2	22.67	9.35	15.83
5	2	2	3	15.34	0.18	10.76
6	2	3	1	35.72	0.31	8.59
7	3	1	3	11.97	0.65	8.69
8	3	2	1	24.68	0.27	5.82
9	3	3	2	30.97	0.26	15.23
CO Conversion	K_{1j} 58.21	56.07	81.83	$K=199.56$		
	K_{2j} 73.73	56.63	70.25	$W=4878.653$		
	K_{3j} 67.62	86.86	47.48	$P=4424.9104$		
	U_j 4465.6605	4631.8205	4628.5206	$Q_T=453.7426$		
	Q_i 40.7501	206.9101	203.6102	$Q_E=2.4722$		
CO ₂ Conversion	K_{1j} 1.44	10.23	0.81	$K=12.46$		
	K_{2j} 9.84	0.9	10.06	$W=88.947$		
	K_{3j} 1.18	1.33	1.59	$P=17.2502$		
	U_j 33.4305	35.7439	34.7959	$Q_T=71.6968$		
	Q_i 16.1803	18.4937	17.5457	$Q_E=19.4771$		
CH ₃ OH time-space yield	K_{1j} 26.62	29.35	19.42	$K=91.54$		
	K_{2j} 35.18	24.54	39.02	$W=1056.2802$		
	K_{3j} 29.74	37.47	33.1	$P=931.0635$		
	U_j 943.5748	959.4111	998.4356	$Q_T=125.2167$		
	Q_i 12.5113	28.3476	67.3721	$Q_E=16.9857$		

Table 3 Variance analysis of CO conversion of straw syngas

Items	Deviations	Freedom	Mean square deviations	F value
Reaction temperature	40.7501	2	20.37505	16.4833
Reaction pressure	206.9101	2	103.45505	83.6947
Entrance flow of syngas	203.6102	2	101.8051	82.3599
Error	2.4722	2	1.2361	
Sum	453.7426	8		

Table 4 Variance analysis of CO₂ conversion of straw syngas

Items	Deviations	Freedom	Mean square deviations	F value
Reaction temperature	16.1803	2	8.09015	0.8307
Reaction pressure	18.4937	2	9.24685	0.9495
Entrance flow of syngas	17.5457	2	8.77285	0.9008
Error	19.4771	2	9.73855	
Sum	71.6968	8		

Table 5 Variance analysis of CH₃OH time-space yield for straw syngas

Items	Deviations	Freedom	Mean square deviations	F value
Reaction temperature	12.5113	2	6.25565	0.7366
Reaction pressure	28.3476	2	14.1738	1.6689
Entrance flow of syngas	67.3721	2	33.68605	3.9664
Error	16.9857	2	8.49285	
Sum	125.2167	8		

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