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Reactions and Technology of Black Liquor Gasification Combined Synthesis of Dimethyl Ether†

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Current research was carried out to develop a technical program for black liquor gasification combined synthesis of dimethyl ether (DME). The chemical reactions and existing technology of black liquor gasification and dimethyl ether synthesis were discussed in detail. Then, bases on the chemical reactions and existing technology, a technical program for black liquor gasification combined synthesis of dimethyl ether was developed, which mainly composed five sections of black liquor gasification, gas desulfurization, CO conversion, synthesis of methanol and synthesis of dimethyl ether. The main technical parameters were chosen as: (1) black liquor gasification: pressure, atmospheric pressure; temperature, 1000 ºC; oxidant, oxygen; mass ratio of oxygen and black liquor, 2-2.5; (2) synthesis of methanol: pressure, 5-7 Mpa; temperature, 227-257 ºC; catalyst: CuO- ZnO-Al_2O_3 or CuO-ZnO-Cr_2O_3; (3) synthesis of dimethyl ether: pressure, 1-2 MPa; temperature, 250 ºC-300 ºC; catalyst: γ-Al_2O_3, H-ZSM-5.

Key Words: Black liquor, Gasification, Synthesis, Methanol, Dimethyl ether.

INTRODUCTION

Pulping black liquor is a viscous liquid produced in the chemical pulping process and belonged to industrial waste[1]. On other hand, contained large amounts of organic contents and heat value of 1.4-1.6 MJ/kg[2], it is a kind of renewable energy resource. For 1.5-1.7 ton dry solid black liquor was produced with producing 1 ton nature dry pulp[3], there was large amounts of black liquor in the pulp mill. In year of 2010, there were about 2005 million tons of new pulp produced in China. About 70 % of that new pulp was produced by chemical pulping process, accompany with 2100-2380 million tons of black liquor liquor produced and those total heat was equivalent to 650-760 million tons of coal[4].

Nowadays, facing the twin challenges of energy shortages and global warming[7], how to effectively use the black liquor has been concern and become a research hot spot. Since dimethyl ether is biomass fuel that is an alternative to petroleum products, black liquor gasification combined synthesis of dimethyl ether has been one of the major industrial applications of black liquor gasification. In year of 2004-2007, a black liquor gasification with oxygen project that processed 12 tons per day of dry solids black liquor was constructed at Kappa Kraftliner, Piteå, Sweden. In year of 2009, the project was further developed to become the first black liquor refining plant in the world, where 4 tons of dimethyl ether was produced in per day[5-7].

Research of black liquor gasification and gas desulfurization has been carried out in China and will be further developed to the research of black liquor gasification combined synthesis of dimethyl ether. Therefore, a technical program of that was required. In this paper, the related chemical reactions and existing technology of black liquor gasification and dimethyl ether synthesis were discussed in detail. Then, bases on the reactions and the existing technology, a technical program for black liquor gasification combined synthesis of dimethyl ether would be developed.

Process of black liquor gasification combined with synthesis of dimethyl ether: Black liquor gasification combined synthesis of dimethyl ether included five sections of black liquor gasification *viz.*, gas desulfurization, CO conversion, methanol synthesis and dimethyl ether synthesis (Fig. 1).

Black liquor was fed into the gasifier after be atomized and mixed with oxygen in an atomizer fixed in the top of gasifier, in which strong black liquor was dried up and a serial reactions of black liquor gasification took place. Those reaction produced ash (residue) and the gasification gas that mainly composed of CO, H_2 and other little amounts of gas. The gasification gas from the gasifier was conducted into a waste heat boiler, in which the high temperature gas was cooled to about 150 ºC in the time low pressure vapour was produced and then the cooled gas was conducted into the desulfurization tower, in which the sulfides was removed by reacted with

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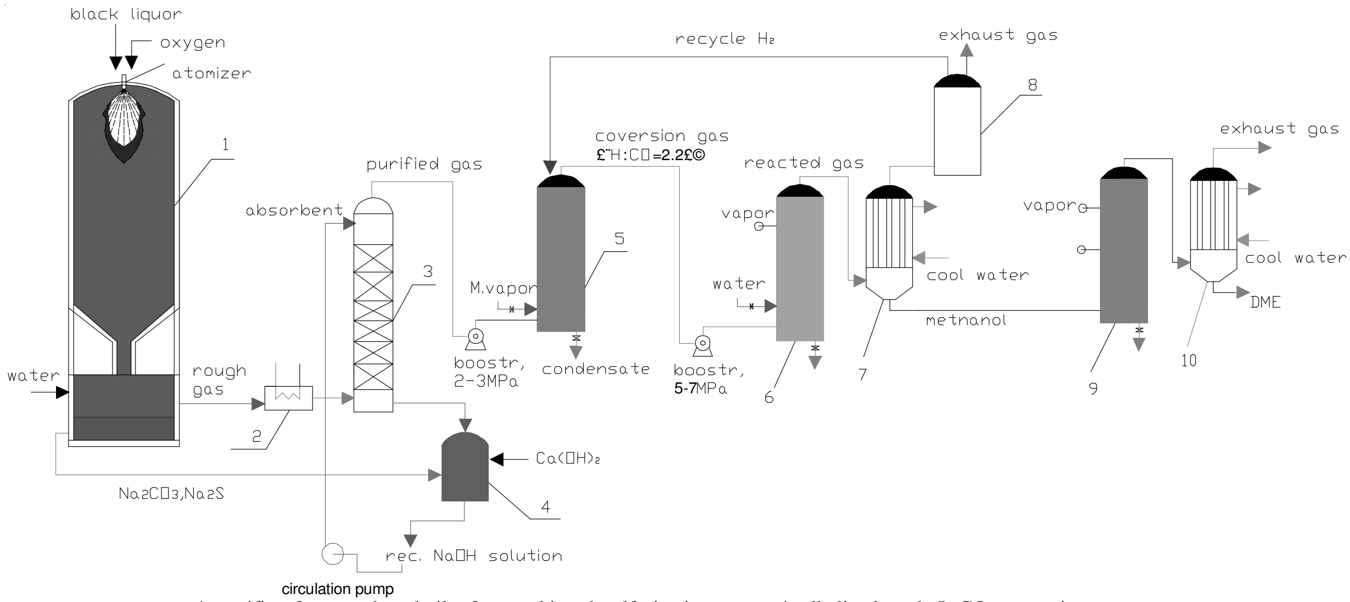

1: gasifier; 2: waste heat boiler;3: a packing desulfurization tower; 4: alkalized pool; 5: CO conversion reactor; 6: methanol synthesis reactor; 7: methanol separator; 8: H_2 separator; 9: DME synthesis reactor; 10:DME separator.

Fig. 1. Flow chart of black liquor gasification combined synthesis of dimethyl ether

NaOH solution. The desulfurization absorption solution contained Na_2CO_3, Na_2S and CH_3SNa was alkalized with $Ca(OH)_2$ to reproduce NaOH that could be recycled as the absorbent of desulfurization.

After desulfurization, the gas was pressurized to 0.1-2 Mpa by a booster and was fed into the CO conversion reactor, in which part of CO reacted with water vapour to produce H_2 and CO_2 and thus the molar ratio raised to $H_2/CO = 2.2$. After conversion, the synthesis gas was pressurized to 5-7 MPa and fed into the methanol synthesis reactor to produce methanol. Then the produced methanol and exhaust gas were cooled and separated in a special methanol separator. The exhaust gas was conducted into a H_2 separator to separate and recycle the H_2 remaining in the exhaust gas. Finally, the methanol was fed into the dimethyl ether reactor to produce dimethyl ether, which was the aim products and was separated in a special dimethyl ether separator.

EXPERIMENTAL

Black liquor gasification

Reactions of black liquor gasification: It was simply divided as four stages of drying, pyrolysis, combustion and reduction in the process of black liquor gasification.

Reactions in the pyrolysis stage: Some components of black liquor were pyrolyzed in 195-255 ºC, produced oily liquid (tar) and gaseous benzene, phenol and ethylene. In 255-590 ºC, pyrolysis was continue, produced decomposition products of lignin macromolecules and small pieces of organic molecules. At 590 ºC, the more pyrolysis products were produced included acetone, 2-methyl-1-butene, acetic acid, 2- methyl-propionaldehyde, hexatriene, hydroxyl ethyl acetate, toluene, *etc*. Those intermediate products mixed together and become the mixture called tar. Further reactions took place between the intermediate components and finally produced CO, CO_2, H_2, CH_4, H_2S and little amounts of CH_3SH and CH_3SCH_3[8-10]. Not considered the complex intermediate reactions and the components in little amounts, based on the first reactants and the final products, the pyrolysis reaction of black liquor was expressed as:

$$NaC_aH_bO_cS_e \rightarrow iC + k\,Na_2CO_3 + l\,CO_2 + m\,CO + n\,H_2 + o\,CH_4 + p\,H_2S + q\,H_2O \quad (1)$$

Reactions in the combustion stage: Inside the gasifier, the pyrolysis products such as small molecules CO, H_2, CH_4 and H_2S diffused to the outer space of particles and combusted with oxygen. When combustion took place in the outer space, for the oxygen molecules was prevented outside the combustion interface, the particles could not met oxygen and combustion did not occur inside the particles temporarily. Strongly heated by external flame, further reactions took place inside the particles to produce gas maintaining the outer flame. Only after depletion of the gas and the outer flame disappeared, the charcoal could meet oxygen and combusted[8,11]. Those combustion reactions were:

$$H_2 + 0.5\,O_2 \rightarrow H_2O \quad (2)$$

$$CO + 0.5\,O_2 \rightarrow CO_2 \quad (3)$$

$$CH_4 + 1.5\,O_2 \rightarrow CO_2 + H_2O \quad (4)$$

$$H_2S + 1.5\,O_2 \rightarrow SO_2 + H_2O \quad (5)$$

$$C + O_2 \rightarrow CO_2 \quad (6)$$

Reactions in the reduction stage: After the combustion reaction (oxygen depleted), mixtures of water vapour, CO_2, H_2, SO_2 and charcoal stayed in the gasifier. At high temperature, the charcoal could reacted with those water vapour, CO_2 and H_2[10,12] and SO_2 and CO_2 could be reacted with H_2. Reactions in the in the reduction stage were:

$$C + H_2O \rightarrow CO + H_2 - 131.5 \text{ kJ/mol} \quad (7)$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 - 90 \text{ kJ/mol} \quad (8)$$

$$C + CO_2 \rightarrow 2CO - 162.4 \text{ kJ/mol} \quad (9)$$

$$C + 2H_2 \rightarrow CH\backslash + 74.9 \text{ kJ/mol} \quad (10)$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_3O \quad (11)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (12)$$

Total reaction equation of black liquor gasification: From reactions (1)-(12), the final gasified completely products concluded CO, CO_2, H_2, CH_4, H_2S, H_2O and Na_2CO_3. Not considered the complex intermediate reaction and the contents in little amounts, based on the first reactants and the final products, the total reaction equation of black liquor gasification with oxygen could be expressed as eqn. (13).

$$NaC_aH_bO_cS_e + f\,O_2 \rightarrow k\,Na_2CO_3 + l\,CO_2 + m\,CO + n\,H_2 + o\,CH_4 + p\,H_2S + q\,H_2O \quad (13)$$

Technology of black liquor gasification: Generally, black liquor gasification was carried out with an ejected gasifier, in which black liquor was fed after be atomized and mixed with oxygen in an atomizer fixed in the top of gasifier[7,13] (Fig. 1).

An oxygen-ejected bagasse black liquor gasification pilot experiment has been taken in year 2006 -2008 at Guangxi University, Nanning, China. The results obtained as: conversion of organic carbon, 89.7-91.0 %; gas constitutes (v %): H_2, 42; CO, 26.7; CO_2, 29.8; CH_4, 0.6; H_2S, 0.63. the gas thermal efficiency was 69.2-78.3 % with concentration of black liquor in range of 60-75 %, corresponding to oxygen ratio of 45-50 % black liquor[13]. The main parameters of oxygen-ejected bagasse black liquor gasification were shown in Table-1.

TABLE-1
MAIN PARAMETERS OF OXYGEN-EJECTED BAGASSE BLACK LIQUOR GASIFICATION

Parameters	
Operation temperature	1000 ºC
Operation pressure	Atmosphere
Oxidant	Oxygen
Concentration of black liquor	60-75 %
Mass ratio between black liquor and oxygen	2-2.5

RESULTS AND DISCUSSION

Gas desulphurization: Current gas desulphurization is mainly alkali absorption method[14], organic amine absorption method[15] and high temperature reaction method[16,17]. The high temperature reaction method is hard to meet the pulp and paper industry for requiring large scale of solid absorbent and making large scale of solid waste in pulp mill. The alkali absorption method and organic amine absorption method are mainly aim at removal of H_2S, does not involve removal of CH_3SCH_3 and CH_3SH.

Black liquor gasification gas contains CO, CO_2, H_2, CH_4 and a small amount of sulfide[2,7,13], including hydrogen sulfide, methyl mercaptan and dimethyl sulfide. For deep desulphurization, a simulating experiment was carried out with ZnO catalyst and NaOH solution as absorbent[18,19]. In the condition of high temperature and ZnO catalyst, dimethyl sulfide and hydrogen reacted to produce methane and sulfide hydrogen, then the sulfide hydrogen was absorbed with NaOH solution. The reaction equations were:

Conversion reaction:

$$CH_2SCH_3 + 2H_2 \xrightarrow{ZnO} 2CH_4 + H_2S \quad (14)$$

Absorption reactions:

$$H_2S + 2\,NaOH = Na_2S + 2H_2O \quad (15)$$

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O \quad (16)$$

Another desulphurization experiment was carried out with a packing absorption tower with NaOH solution as absorbent. H_2S and CH_3SH were removed by reacted with NaOH solution. Although CH_3SCH_3 be not removed and still stayed in gas, in low concentration of 2-6 mg/L and little affected to the sulfur-resistant catalysis[20], the desulfurization gas could be use as the feed gas for reaction of CO conversion and methanol synthesis. The reaction equations were:

$$H_2S + NaOH = Na_2S + H_2O \quad (15)$$

$$CH_3SH + NaOH = CH_3SNa + H_2O \quad (17)$$

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O \quad (16)$$

The main parameters of desulphurization are shown in Table-2.

TABLE-2
MAIN PARAMETERS OF DESULPHURIZATION

Parameters	
Operation temperature	38-45 ºC
Operation pressure	Atmosphere pressure
Absorbent	NaOH solution
Temperature of feed solution	30 ºC ≤

CO conversions: After desulfurization, the synthesis gas mainly composed of H_2 and CO, where the molar ratio was about $H_2/CO = 1.64$[3,7,13]. For the optimal molar ratio of H_2 and CO was 2.2 in the synthesis reaction of methanol, part of CO should be reacted with water vapour to produce H_2 and CO_2 and thus the molar ratio of H_2 and CO raised to $H_2/CO = 2.2$. The reaction of CO conversion was:

$$CO + H_2O \xrightarrow{catalyst} H_2 + CO_2 - 40.9\ kJ/mol \quad (18)$$

CO conversion was carried out with a special CO conversion reactor[21-23], in which a lot of reaction tubes arranged to form a larger volume of reaction space. The catalyst was fed inside the tubes, where the CO conversion reaction took place in the time mixed gas of CO, H_2 and vapour went through. It was an empty space outside the tubes, where the excess heat of reaction was spread out with a flow vapour.

It was volume ratio 38.8-42.45 % of H_2 and 29.78-38.48 % of CO in black liquor gasification gas, in which need only about 20-30 % of CO conversion to change the ratio from 1.64 to 2.2. For the low conversion ratio of CO, the reaction heat was not large enough to raise the catalyst bed to high temperature. So, a low-temperature conversion process could be chose, which main parameters of CO conversion are shown in Table-3.

TABLE-3
MAIN PARAMETERS OF CO CONVERSION

Parameters	
Operation temperature	190-250 ºC
Operation pressure	0.1-3 MPa
Catalyst	Copper-zinc catalyst

Synthesis of methanol: Methanol was mainly synthesized in gas state in current industry. The reactions were:

$$CO + 2H_2 \xrightarrow{catalyst} CH_3OH + Q \quad (19)$$

$$CO_2 + 3H_2 \xrightarrow{catalyst} CH_3OH + H_2O + Q \quad (20)$$

Side reaction:

$$CO_2 + 3H_2 \xrightarrow{catalyst} CH_4 + H_2O - Q \quad (21)$$

In the methanol synthesis reaction, the feed gas mainly composed of CO and H_2 and a little amount of the CO_2, N_2 and CH_4 were allowed. The catalysts were mainly copper-zinc catalysts dispersed in the carrier of Cr_2O_3 or Al_2O_3, just as CuO-ZnO -Cr_2O_3 and CuO-ZnO-Al_2O_3 catalyst[24,25].

Methanol synthesis was carried out with a special methanol synthesis reactor. Many kind of methanol synthesis reactor has been developed and applied in the industry. The active temperature of CuO-ZnO-Cr_2O_3 catalyst was in range of 500-530 K, with pressure of 5-7 MPa[26]. The methanol synthesis reactions were exothermic reactions, that the exothermal could raise the temperature of catalytic bed and maybe caused catalyst deactivation or accelerated the rate of side reaction. So, a serial cooling devices was required in the methanol synthesis reactor.

Followed with the methanol synthesis reactor, the produced methanol and exhaust gas were conducted into a special methanol separator, in which the mixtures of gas were cooled indirectly to about 32-38 ºC with cool water. At which temperature methanol was condensate and become liquid and then was discharged from the liquid outlet. Contained volume ratio 60-70 % of H_2, the exhaust gas was conducted into a H_2 separator filled with special organic polymer membrane to separate and recycle the H_2. The main parameters of methanol synthesis are shown in Table-4.

TABLE-4
MAIN PARAMETERS OF METHANOL SYNTHESIS

Parameters	
Reaction temperature	200-290 ºC
Reaction pressure	5-7 Mpa
Catalyst	CuO-ZnO-Cr_2O_3
Molar ratio H_2/CO	2.2
Cool water temperature	5-11 ºC
Methanol separator operating temperature	32-38 ºC
H_2 separator operating temperature	65 ºC
Pressure of input exhaust gas	7.45 Mpa
Pressure of penetrated H_2	5.45 Mpa

Synthesis of dimethyl ether: Synthesis of dimethyl ether from methanol may reacted in gas state that the vapour of methanol was conducted through an acid catalytic layer, where methanol was dehydrated and dimethyl ether was produced[27,28]. The acid Catalysts were Al_2O_3 or crystalline Al_2 $(SiO_3)_3$. The reaction was (2) and the main parameters are shown in Table-5.

$$3CH_2OH \xrightarrow{\text{catalyst}} CH_2OCH_3 + 2H_2O - 21.255 \text{ kJ/mol} \quad (22)$$

TABLE-5
MAIN PARAMETERS OF SYNTHESIS
OF DME IN LIQUID STATE

Parameters	
Reaction temperature	250 - 300 ºC
Reaction pressure	1-2 MPa
Catalyst	γ - Al_2O_3, H-ZSM-5

Conclusion

Based on the chemical reactions and existing technology, a technical program for black liquor gasification combined synthesis of dimethyl ether has been developed, in which black liquor was gasified at high-temperature to produce synthesis gas, then by part conversion of CO, synthesis of methanol and synthesis of dimethyl ether, dimethyl ether could be prepared. The main technical parameters were chose as: (1) black liquor gasification: pressure, atmospheric pressure; temperature,1000 ºC; oxidant, oxygen; mass ratio of oxygen and black liquor, 2-2.5. (2) Synthesis of methanol: pressure, 5-7 Mpa; temperature, 227~257 ºC; catalyst: CuO- ZnO-Al_2O_3 or CuO-ZnO-Cr_2O_3. (3) Synthesis of dimethyl ether: pressure, 1-2 MPa; temperature, 250-300 ºC; catalyst: γ-Al_2O_3, H-ZSM-5.

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