# Integrated Analysis of Energy, Economic, and Environmental Performance of Biomethanol from Rice Straw in China

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This paper focuses on a biomethanol from the rice straw process involving the thermodynamic, economic, and environmental performance in China. Based on the simulation of methanol synthesis via biomass gasification in interconnected fluidized beds using Aspen Plus software, the method of LCA (Life Cycle Assessment) is applied to evaluate the impact of pollutant emissions in the full life cycles of biomethanol. The integrated performance of biomethanol system is analyzed combining with energy utilization, economic cost, and environmental impact. The results show that the methanol yield can reach 0.308 kg/(kg rice straw), i.e., the energy efficiency of rice straw conversion to biomethanol is approximately 42.7%. For a biomethanol plant with an annual production of 50,000 tons, the real cost of biomethanol is evaluated at 2685 RMB/t, in which the economic cost is 2347 RMB/t, and the environmental cost is 337.6 RMB/t. Because of its high investment cost, presently the economic cost of biomethanol is higher than that of coal-based methanol in China. Nevertheless biomethanol will be becoming more competitive with the shortage of fossil fuel in the future. In the whole life cycle, the main pollutant emissions come from the biomethanol production process and biomethanol end-use by automobiles, whereas the net environmental effect is negative during the rice cultivation. Global warming is the most influential factor of the different impact categories. However, 1910 kg of CO<sub>2</sub> can be fixed for one ton of methanol by photosynthesis in the growth of rice, thus the effect of global warming is significantly reduced by biomass utilization compared with coal-based methanol. The integrated performance indicates that producing methanol from rice straw is beneficial to both the utilization of agriculture waste and in the improvement of environment.

#### 1. Introduction

Biomass is considered as a potential feedstock for alternative liquid fuels due to the problem of fossil fuel depletion worldwide. One of the important ways is that of methanol (MeOH), dimethyl ether (DME), and biodiesel for automotive fuel via biomass gasification and synthesized. In China, there are abundant biomass resources, including crop residues, forest refuses, and municipal solid wastes, etc. According to the report, the total amounts of biomass recourses are 700 million to to (ton coal equivalent) per year, and available crop residues are estimated at 120 million to for energy utilization. Among them, rice straw approximately makes up one-fourth of the total amount.

In the 1980s, research on the synthesis of methanol and dimethyl ether via biomass was carried out in the developed countries such as U.S.A., Japan, and EU Countries.<sup>3</sup> Recently, this indirect biomass liquefaction has attracted more attention around the world.<sup>4–8</sup> The technological process of producing biomethanol, including biomass gasification, gas reform and catalytic synthesis, has been achieved in the laboratory by the Guangzhou Institute of Energy Conversion of China.<sup>9–11</sup> In addition, other research institutes, such as the University of Science and Technology of China, Zhejiang University, etc., also carry out the related research.<sup>12,13</sup>

The reason for developing biomass technology for methanol is that it can not only provide alternative fuel for automobiles but also the conversion of biomass to biomethanol can reduce environment burden. With the development of the technical research, the integrated performance analysis of the biomethanol process is required for commercialization in the future.

Life cycle assessment (LCA) is a method for determining the environmental impact of a product during its whole process, thus it is a good tool for quantifying environmental impacts of a renewable energy utilization system. Several LCA studies focusing on the advanced biomass conversion technologies have been conducted, including biomass gasification, combustion, and liquefaction. <sup>14–17</sup> Recently, LCA for biomass diesel, methanol, and ethanol also has been evaluated. <sup>18–22</sup> However, the analysis of energy efficiency and economic feasibility together is concerned less with life cycle assessment of environmental impact in the previous studies.

This paper focuses on a biomethanol fuel from rice straw involving the thermodynamic, economic, and environmental performance in China. The method of LCA is applied to evaluate the impact of pollutant emissions in the full life cycles of biomethanol. In addition, the performance of biomethanol production system is analyzed combining with energy utilization, economic cost, and environmental impact.

## 2. System Simulation and Thermodynamic Performance

**2.1. System Configuration.** In this paper, a process system of methanol synthesis via biomass gasification in interconnected fluidized beds is adopted.<sup>23</sup> The system configuration is illustrated in Figure 1 taken from ref 23.

The proposed gasification technology of interconnected fluidized beds resembles a circulating fluidized bed with the extra bubbling fluidized bed after the cyclone. The circulating fluidized bed is designed for combustion fed with air; the bubbling fluidized bed for biomass gasification is fed with steam. Direct contact between the gasification and combustion processes is avoided; the gasification-required heat is achieved by means of the circulation of bed particles (such as sand, catalyst). One part of biomass is rapidly pyrolysis and gasified with steam

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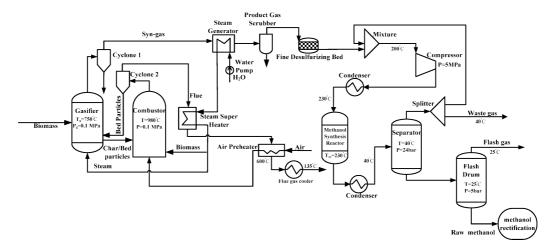


Figure 1. System process of methanol synthesis via biomass gasification in interconnected fluidized beds.

to produce syngas, including H2, CO, etc. in the bubbling fluidized bed. The unreacted char with bed particles is backpassed into the circulating fluidized bed, where the additional biomass is also fed to burn together with the unreacted char and the bed particles mass a great deal of heat. The hot bed particles are separated from flue gas and returned to the gasifier to provide heat needed for biomass gasification.

For the purpose of improving hydrogen yield and tar decomposition, CaCO3 is added into the inert bed particles based on previous works, 24-27 which have revealed that the calcined CaCO<sub>3</sub> could act as an effective catalyst for carbon conversion with reducing tar emission in biomass gasification, especially for steam gasification. The results showed that carbon conversion of biomass could reach 96.95%, and tar content could be controlled 1-5 g/m³ gas. 24,25,27 The slight residual tar can be removed by the cleanup unit in the system. On the one hand, CaCO<sub>3</sub> could be used to effectively reduce tar in the biomass gasifier with steam. On the other hand, CaCO3 used as the additive for bed material could circulate between the gasifier and the combustor. The gasifier is at 750 °C, and the temperature of the combustor is maintained at the range of 900-980 °C, and consequently these CaCO<sub>3</sub> can be calcined and turned into CaO in the combustor. After being calcined, the CaO returned to the gasifier can help to absorb CO<sub>2</sub> and result in affecting gasification equilibrium and adjusting the proportions of H<sub>2</sub> and CO in the gas product. The produced CaCO<sub>3</sub> from the gasifier would decompose and release CO2 again when back to the combustor, so that the regeneration cycle of CaO can be carried out in the interconnected fluidized beds. Furthermore, the calcined CaCO3 as sulfur sorbent in the gasifier could remove the sulfur in the product gas. <sup>28,29</sup> The suggestions of CaCO<sub>3</sub> as sorbent for removing  $CO_2$  and sulfur also have been studied by other researchers.  $^{30-33}$ 

Prior to feeding to the methanol synthesizer, product gas from the biomass gasification in interconnected fluidized beds has to be cleaned up and separated to satisfy the synthesizer requirement. After purge and separation, biomass syngas is compressed at a high pressure and fed into the synthesizer. The reactions of methanol synthesis occur at the catalyst layer of the synthesizer. The outlet gas, including methanol, steam, and some unreacted gases such as H<sub>2</sub>, CO, CO<sub>2</sub>, and inert gases (N<sub>2</sub> and CH<sub>4</sub>), are refrigerated by the water cooler where methanol and water are condensed. Then the gas and liquid are separated in the separator. The separated crude methanol sends off the dissolved gas to the flasher. After that, it is passed into the further rectification section. The gas from the top of the separator goes

through the splitter with part emission. Most of the gas is circulated and compressed with the fresh biomass syngas to react in the synthesizer. The rest of the gas with inert gases gives off to maintain the pressure of the whole system.

**2.2. System Simulation.** The process simulation of methanol synthesis via biomass gasification in interconnected fluidized beds was carried out using Aspen Plus in our previous study,<sup>23</sup> which was another part of the study. In order to clearly analyze the integrated performance of the system, the simulation of the biomass methanol production is reported briefly in the present paper. The models and results of the simulation are all based in ref 23.

The whole system could be regarded as the combination of three subsystems, i.e., the gasification subsystem, where the biomass is converted into raw syngas; the cleanup subsystem, where the impurities contained in the raw syngas are removed; and the synthesis system, where the biomass syngas is converted into liquid methanol. Aspen Plus software is applied to establish the models of the biomass gasification process on the basis of principles of mass, chemical, and energy balance and the methanol synthesis process on the basis of the chemical kinetics.

**2.2.1. Gasification Model.** The biomass gasification subsystem consists of two reactors, a gasifier and a combustor, thus the gasification model consists of two modules, a gasification module and a combustion module. The models of gasifier block used to simulate the biomass gasification process in the bubbling fluidized bed and combustor block used to simulate biomass combustion process in the circulating fluidized bed are both on the basis of the principle of minimization of Gibbs' free energy, which originated from Rgibbs block of Aspen Plus.

In the simulation, the assumptions of the model are made as follows:

- (1) The combustor and the gasifier were operated under a steady state, and residence time was long enough for the reactions to reach chemical equilibrium.
- (2) Ash in biomass as well as in bed particles (sand) was inert and did not participate in chemical reactions.
- (3) The product gases of biomass gasification were CO,  $H_2$ , CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, COS, and SO<sub>2</sub>; tar was not taken into account in the simulation.
- (4) The pressure loss in the combustor and the gasifier was not taken into account in the simulation.
- (5) The reactor temperature was uniform and there is no temperature gradient.
- **2.2.2.** Clean-up Model. The raw syngas from the gasifier contains some impurities, such as H<sub>2</sub>S, COS, HCN, NH<sub>3</sub>, tar,

etc. In order to avoid the Cu-based catalyst deactivation in methanol synthesis, the impurities must be removed from the syngas before entering the methanol sythesis reactor. The removal of the particulate in the raw syngas is achieved by a cyclone and a midtemperature ceramic filter. Alkali metals condense at a temperature lower than 500 °C and thus can also be removed with the particulate.<sup>34</sup> The residual tar is trapped by a condensing unit. The sulfur compound is separated by means of dry desulfurization with ZnO, by which the sulfide in the syngas could be reduced to 0.05 ppm, at the temperature of less than 400 °C.<sup>35</sup> As ZnO is one kind of effective low-temperature H<sub>2</sub>S adsorbent, it has been widely used as an H<sub>2</sub>S removal agent from natural gas and gasified fuel gases in the integrated gasification combined cycle (IGCC) and fuel cells (FCs) system.

In the simulation, the standard unit operation model, Sep block from Aspen Plus, is used for simulating the cleanup units, which reduce all impurity concentrations to the value allowed for the methanol synthesis. So the impurities of the syngas, such as H<sub>2</sub>S, COS, HCN, and NH<sub>3</sub>, etc., after purification, are not considered in the methanol synthesis.

**2.2.3.** Liquefaction Model. Typical gas-phased Lurgi methanol synthesis is applied to the process of converting biomass syngas to liquid methanol in this paper. The main reactions involved in the liquefaction process are as follows

$$CO + 2H_2 \rightarrow CH_3OH -90.6 \text{ kJ/mol}$$
 (1)

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O -49.5 \text{ kJ/mol}$$
 (2)

$$CO + H_2O \rightarrow CO_2 + H_2$$
 -28.6 kJ/mol (3)

The pipe catalytic reactor with heat transfer for methanol synthesis is adopted, which originated from the Rplug block of Aspen Plus. In the block, the global reaction rates of (1) and (2) are simulated by Langmuir—Hinshelwood—Hougen—Watson (LHHW) global kinetic models.

The following assumptions for liquefaction model are made based on the application of Aspen Plus software:<sup>36</sup>

- (1) Five components of the biomass syngas, consisting of CO,  $H_2$ ,  $CO_2$ ,  $CH_4$ , and  $N_2$ , were taken into account, in which  $N_2$  and  $CH_4$  were inert.
- (2) Pressure loss in the methanol synthesizer was not taken into account.
- (3) Material gas is sufficiently preheated, and temperatures in the methanol synthesizer were assumed to be uniform.
- (4) Gas phase in the methanol synthesizer was supposed to be flat stream and no back-mixing exists.

Flash2 block in Aspen Plus can be used to simulate flash drum, evaporator, liquid separate pot, and other single-stage separators. Given that, Flash2 block of Aspen Plus is adopted, serving as the separator and flash tank. It performs the function of simulating the process of the two-phase gas—liquid separation.

- **2.3.** Process Calculation and Thermodynamic Performance Analysis. **2.3.1.** Process Calculation Basis and Conditions. The biomass studied in the paper is the rice straw from Jiangsu Province, China. The proximate analysis and the ultimate analysis of biomass are shown in Table 1, and the general process calculation basis and conditions are given in Table 2.
- **2.3.2.** Thermodynamic Performance Results and Discussion. Based on the basis calculation of Tables 1 and 2, the results of system thermodynamic performance are shown in Table 3.

Table 1. Proximate Analysis and Ultimate Analysis of Biomass

proximate analysis (wt %)		ultimate analysis (wt %)	
moisture	9.1	С	35.37
fixed carbon	16.75	Н	4.82
volatile	63.69	O	39.15
ash	10.46	N	0.96
low heating value (MJ kg <sup>-1</sup> )	14.4	S	0.14

Table 2. Input Data for System Simulation

parameter	value
biomass feed rate	3600 kg/h
gasification temperature	750 °C
steam/biomass ratio	0.4
combustor temperature	980 °C
air flow rate	2.2 kg/s
air inlet temperature	20 °C
feed water inlet temperature	20 °C
CaCO <sub>3</sub> /biomass ratio	1.5
carbon conversion of biomass	99%
outlet cold fuel gas temperature	135 °C
heat loss	3% of input heat
specific heat volume of bed particles (sand)	1.2 kJ/(kg•°C)
liquefaction temperature	230 °C
liquefaction pressure	5 MPa
proportion of the circle gas	0.97

Table 3. Thermodynamic Performance of the Biomethanol System

case	results
mole fraction of syngas in the gasifier	
$H_2$	59.44%
CO	23.95%
$CO_2$	15.9%
$CH_4$	0.20%
$N_2$	0.51%
dry gas yield of biomass gasification	$1.05 \text{ m}^3/\text{kg}$
cold gas efficiency	69.5%
mole fraction of flue gas in the combustor	
$\mathrm{O}_2$	7.27%
$N_2$	68.9%
CO	0.03 ppm
$CO_2$	12.6%
$H_2O$	11.1%
$SO_2$	1.02 ppm
NOx	175 ppm
flue gas flow	8.29 m <sup>3</sup> /kg
biomass ratio of gasifier to combustor	2.3
methanol yield	0.308 kg/kg rice straw
ash	0.105 kg/kg rice straw

As shown in Table 3, the main compositions of the gasifier syngas are H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> (excluding H<sub>2</sub>O). Hydrogen content is nearly 60%, and the hydrogen/carbon ratio (H<sub>2</sub>/ (CO+1.5CO<sub>2</sub>)) and the CO<sub>2</sub>/CO ratio are 1.2 and 0.66, respectively. However, hydrogen content is generally 21%-38% in the case of air or oxygen gasification of biomass in a fluidized bed, and the hydrogen/carbon ratio is only 0.25–0.55.<sup>37</sup> Thus, compared with air and oxygen gasification of biomass, the composition of production gas from biomass gasification in the interconnected fluidized beds is more favorable to synthesis methanol. From energy conversion efficiency, the conversion efficiency of rice straw to methanol is approximately 42.9%, and the methanol yield can reach 0.308 kg per kilogram of rice straw, i.e., its consumption rate is 3.25 kg of rice straw per kg of methanol. At present, the coal consumption of coal-based methanol is approximately 1.4 kg standard coal per kg of methanol.<sup>38</sup> That is, the conversion efficiency of coal is 48.8% for the scale of an annual output of 600,000 ton of methanol in China. It can be seen that the energy efficiency of biomethanol is less than that of the coal-based methanol. One reason is that the energy density of biomass is lower than the coal, so it results in a decrease of the energy conversion efficiency. On the other

Table 4. Basic Data for Economic Performance Calculation

case	value	
credit interest rate	6.12%	
construction credit ratio	70%	
depreciation years	15 years	
operation hours per year	6000 h	
maintenance	3% of fixed assets	
rice straw price	250 RMB <sup>a</sup> /t	
limestone price	100 RMB/t	
catalyst price	100 RMB/kg	
electricity price	0.5 RMB/kWh	
staffing	120 persons	
average wages of staff	40000 RMB/person/year	

<sup>&</sup>lt;sup>a</sup> RMB is the abbreviation for Renminbi, the currency of the People's Republic of China.

Table 5. Economic Performance of Biomethanol Production

case	unit	value
annual production	tons	50,000
investment cost	million RMB	394
economic cost of biomethanol production	RMB/t	2347
(1) raw material cost	RMB/t	1046
(2) depreciation cost	RMB/t	479.9
(3) operation and maintenance cost	RMB/t	584.6
(4) financial cost	RMB/t	68.0
(5) others	RMB/t	168.1

hand, the scale of biomethanol production is smaller due to the economic performance of biomass transportation, and byproducts (such as sulfur, ammonia) of the system have not been taken into account in this simulation, thus the energy losses of the overall system will increase compared with the available coal-based methanol plants.

## 3. Analysis of Economic Performance

**3.1. Basic Data of Economic Calculation.** Based on the thermodynamic analysis of the biomethanol production system, the product cost of the biomethanol is also estimated in this study.

Besides the thermodynamic parameters being based on the above calculation basis and results of simulation, the other assumptions for economic calculation are made as follows:

- Considering the distribution of biomass resources in China, <sup>39</sup> the methanol plant scale would be 50,000 t/a, and the annual operation hours would be 6000 h (=250 day\*24 h). Under these conditions, the product amount of methanol would be 8.3 t/h, and rice straw consumption would be 27.0 t/h, i.e. 162,500t/a.
- The investment cost of the biomethanol system was referred to the related equipment cost and construction cost, etc., of the coal-based methanol plant in China. 40,41
- The price of rice straw included the transportation cost from the agriculture field to the methanol production plant.

With the main parameters of refs 40-43, the other basic data for economic performance calculation are given in Table 4.

**3.2. Economic Performance Results and Discussion.** The results of economic performance are reported in Table 5. The results show that the cost of the methanol product is evaluated 2347 RMB/t. The raw material cost including rice straw, catalyst, and sorbent is the dominating cost factor, accounting for 44.6% of the total cost. On the other hand, the depreciation cost is another important cost factor, accounting for 20.4%. The main reason is that the scale of the biomethanol plant is usually restricted by the amount of straw in the range of the economic collection radius, so that the unit investment cost reaches 7880 RMB/t. As for the annual production capacity of 300,000 tons of the coal-based methanol plant in China, the unit investment

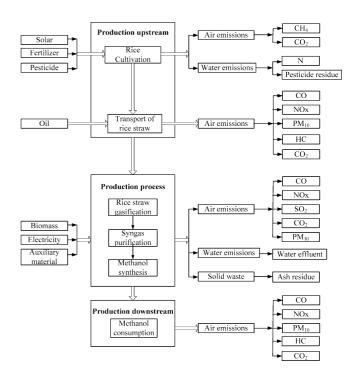


Figure 2. Scope and inventory of LCA for biomethanol.

cost was 5186RMB/t. Furthermore, the cost of the coal-methanol product was 1543 RMB/t at the coal price of 500 RMB/t in 2005. 40 Hence, the unit investment cost of biomethanol is increased by approximately 34% compared with coal-based methanol under the same scale. The results indicate that the coal-methanol has an obvious advantage in investment cost due to its larger scale production. However, the cost of coal-based methanol production will significantly increase with the coal price. The cost of coal-based methanol will be 2393 RMB/t at the coal price of 750 RMB/t, while other conditions keep unchanged. Therefore, biomethanol will be becoming more competitive when the shortage of fossil fuel is more serious in the future.

#### 4. Life Cycle Assessment of Biomethanol

**4.1. Methodology.** Life cycle assessment (LCA) is a method for determining the environmental impact of a product during its entire life cycle - from the raw material acquisition, manufacturing, and use to disposal, so it is a good tool for quantifying environmental impacts of a product system.

The LCA methodology consists of four interrelated components: goal definition and scoping, inventory analysis, impact assessment, and interpretation (ISO 14040, 1998). <sup>44</sup> Each step is described with regard to this study as follows.

**4.1.1. Goal Definition and Scoping.** The first step of life cycle assessment is the goal and scope definition. The aim of this work is to evaluate the environmental impact of the rice straw conversion to methanol fuel in its whole life cycle, to investigate the magnitude of the different pollution categories, and to identify the contributions of the different life cycle phases to the overall impacts. Furthermore, the assessment results can offer the references for the technology selection on liquid fuels from biomass in China.

For the system of methanol synthesis via biomass gasification, the process of energy conversion is a key stage to determine the scope of life cycle assessment in the paper. As shown in Figure 2, the scope of the life cycle includes the following:

Production upstream: biomass cultivation and transportation;

Table 6. Inventory Results of Biomethanol (Per Ton of Biomethanol)

	inventory results of biomethanol (per ton of biomethanol)				
pollutant	rice cultivation	transportation of rice straw	methanol production	methanol consumption	
N	1.6 kg				
pesticide	165 g				
CH <sub>4</sub>	45.2 kg		0.234 kg		
$CO_2$	-1910  kg	13.43 kg	1830 kg	919.25 kg	
HC	_	3.9 g	_	1043.5 g	
CO		48.8 g	1.12 kg	11242.2 g	
NOx		35.1 g	0.928 kg	869.6 g	
$PM_{10}$		5.53 g	0.93 kg	310.6 g	
$SO_2$		C	0.524 kg	C	
slag			410 kg		
water effluent			1000 kg		

- Production process: methanol production including biomass gasification, raw syngas purification, catalytic synthesis, and methanol distillation;
- Production downstream: methanol consumption as automobile fuel.
- **4.1.2. Inventory Analysis.** An inventory analysis of the system is the identification and quantification of raw materials inputs, product outputs, energy inputs and outputs, and pollutant emissions. A traditional inventory quantifies three categories of environmental releases: air emissions, water effluents, and solid waste are taken into account. In this study, the investigated biomethanol system and pollutant emissions considered are illustrated in Figure 2.

The data collection and assumption of the life cycle are obtained and defined in this step. Data concerning the demand for fertilizers and pesticides, energy consumption of transport, and pollutant emissions during the production upstream and downstream processes are taken from refs 45–49 and national statistical data of China. <sup>50,51</sup> For the production process, the inventory data of both rice straw consumption and the emissions come from the above Aspen Plus simulation of the biomethanol production system. According to the considered processes of the life cycle shown in Figure 2, the inventory analyses of the biomethanol during its full life cycle are performed in the following. The functional unit for the evaluation of the life cycle is 1000 kg of biomethanol.

**Rice Cultivation.** Rice straw is taken as the raw material in this study. The environmental impact in the period of rice growth was seldom taken into account, because rice straw tended to be regarded as agriculture waste in the previous studies.<sup>52</sup> In order to investigate the overall environmental impacts of the life cycle, the pollutant emissions from rice cultivation are also taken into account in this paper, considering rice straw is one energy resource when it is used for liquid fuel.

In rice straw growth, the environmental impacts are considered as follows:

- (1) The fertilizer application led to an exceeding value of the total nitrogen and phosphorus in water body and caused water eutrophication. Based on the literature survey in China, 45,50 the most effect on water eutrophication from the paddy field was the nitrogen (N), thus the nitrogen was mainly taken into account in this paper.
- (2) The pesticide residues caused ecotoxicity pollution to water and soil.
- (3) The greenhouse gas, including  $CH_4$  and  $N_2O$ , discharged from the rice paddy field and photosynthetic carbon fixation in rice growth. The  $N_2O$  was considered to be negligible compared with  $CH_4$ .

The system under investigation is assumed to be located in the Jiangsu province of China. The yield of rice straw is assumed to be 0.56 kg/m<sup>2</sup> on the basis of the national statistics of China. <sup>42</sup>

The emission factors for the use of fertilizers and pesticides in the paddy fields are retrieved from refs 45–47 and 51. The data of the greenhouse gas emissions and carbon fixation are calculated from refs 53 and 54. Considering the objective of cultivating rice is for the production of food, the weight of pollution influence between rice straw and rice grain is distributed according to the ratio of the two economic values. The environment impact coefficient allocated to rice straw is calculated as

$$K_{\rm rs} = \frac{MF_{\rm rs} \times P_{\rm rs}}{MF_{\rm rs} \times P_{\rm rs} + P_{\rm rg}}$$

where  $K_{rs}$  is the environment impact coefficient allocated to rice straw;  $MF_{rs}$  is the ratio of the yield of rice straw to rice grain, which is 0.9;  $P_{rs}$  is the price of rice straw, which is 250 RMB/t; and  $P_{rg}$  is the price of rice grain, which is 1540 RMB/t.

The inventory results are listed in Table 6. As shown in Table 6,  $CO_2$  is taken out of the atmosphere during the growth of the rice, while  $CH_4$  emissions are from the rice paddy field.

**Transportation of Rice Straw.** There are many ways to transport the rice straw from the cultivation field to the methanol plant. Considering the economic distance of transportation due to low density of biomass, the main assumptions are made as follows:

- (1) The rice straw transportation average distance was 50 km, covered by trucks.
  - (2) The trucks consumed only diesel.
- (3) The unit diesel consumption was  $0.036\,L/(t\,km)$ , and the density of diesel was  $0.85\,kg/L$ .
- (4) The atmospheric emission pollutants, including HC, CO, NOx, PM<sub>10</sub>, and CO<sub>2</sub>, were considered.
- (5) The fuel consumptions and atmospheric emissions were calculated according to GB18352.3-2005 of China.<sup>48,49</sup>

The emissions for the transportation of rice straw are shown in Table 6.

Methanol Production Process. For the methanol production process, environment pollutants of atmospheric emissions, water effluents, and solid wastes are considered. The main pollutants of atmospheric emissions included CO, NOx, SO<sub>2</sub>, PM<sub>10</sub>, greenhouse gas CO<sub>2</sub>, and CH<sub>4</sub>. The solid waste is mainly from biomass ash. The inventory data of both rice straw consumption and the emissions of atmospheric and solid come from the above simulation results of the biomethanol system. The water effluents are assumed to be treated before discharge, in addition, the amount of water effluents and the pollutant content meet the discharge requirement of industry water (GB8978-1996 of China).<sup>55</sup> The inventory results of this unit process are shown in Table 6.

**Biomethanol Consumption.** The end-use of the biomethanol is considered to be consumed as automobile fuel. According to

the characteristics of automobiles in China, <sup>48,49</sup> the assumptions of this process are as follows:

- (1) The pollutant emissions and fuel consumption were calculated according to 100% methanol-fuel automobile.
- (2) The fuel combustion engine efficiency of methanol-fuel car was equal to that of a car fueled by gasoline. The consumption of a methanol automobile was 16.1 kg/100 km.
- (3) The emission pollutants, including HC, CO, NOx, PM<sub>10</sub>, and CO<sub>2</sub>, were considered. The amount of pollutant emissions from methanol-fuel automobile was obtained from ref 56.

The inventory results of the biomethanol fuel consumption are reported in Table 6.

**4.2. Environment Impact Assessment and Interpretation.** The amount of different pollutants can be observed from inventory data of the whole biomethanol life cycle in Table 6. However, the various pollutants have different environmental impact and damage. According to the method of the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, <sup>53</sup> the pollutant emissions of the system are divided into different impact categories, so as to evaluate how much contributions the various pollutants are and in which process the environmental impact is the most significant of the life cycle.

In this study, seven impact categories are considered: global warming, acidification, photochemical ozone formation, nutrient enrichment, dust and ash, ecotoxicity, and solid waste. In order to evaluate the integrated economic and environmental performance of the system, the environmental potentials of pollutant emissions are characterized by a monetary environmental value, which are mainly estimated on the basis of the environmental value of the pollutants published in ref 57, the economic losses of the different environment pollution, <sup>42,59–61</sup> and the equivalent factors of the pollutants. <sup>18,53</sup>

**Global Warming.** As shown in the previous study on greenhouse effect, <sup>58</sup> the economic loss of global warming approximately accounts for 2.0-9.0% of GDP in the developing countries. According to this suggestion, the economic loss of the global warming effect was assumed to be 4.5% of GDP, in which  $CO_2$  occupied approximately 50% in China. As  $CO_2$  total released 20.5 billion tons (data from EIA), and the total GDP was  $7.09 \times 10^4$  billion RMB from 2001 to 2005, <sup>42</sup> the monetary environmental value of global warming was estimated to be 80 RMB/(t  $CO_2$ ). The global warming effects from  $CH_4$  and NOx were calculated based on the equivalent factors of 25 and 320 compared with  $CO_2$ , respectively. <sup>18,53</sup>

**Acidification.** Substances SO<sub>2</sub> and NOx were considered to cause an acidification impact on the environment. Among them, SO<sub>2</sub> is the most serious acidification pollutant in China. According to preliminary statistics, <sup>42,59</sup> the SO<sub>2</sub> emission was 19.80 million tons/a on average and caused the economic losses, including agriculture damage, forestry destroy, material corrosion, and human health damage, etc., more than 110 billion RMB per year. The monetary environmental value of SO<sub>2</sub> was estimated to be 6000 RMB/t. This result was also consistent with ref 57. The acidification impact of NOx was estimated to be 4200 RMB/t according to the corresponding equivalent factors between SO<sub>2</sub> and NOx, which were 1.0 and 0.7. <sup>18,53</sup>

**Photochemical Ozone Formation.** CO, HC, and NOx were considered as the main contributors to photochemical ozone formation in this paper. The effect equivalent factors of CO and HC on photochemical ozone formation are 1.0 and 20 referred to in ref 53. Based on the monetary environmental value of CO evaluated to 1000 RMB/t in ref 57, and the corresponding characterization factors of CO and HC, the monetary environ-

**Table 7. Impact Categories and Monetary Environmental Values of Pollutants** 

pollutant	impact category	monetary environmental value (RMB/(t pollutant))
$CO_2$	global warming	80
$CH_4$	global warming	1680
NOx	acidification	4200
	photochemical ozone formation	3800
	global warming	25600
$SO_2$	acidification	6000
CO	photochemical ozone formation	1000
HC	photochemical ozone formation	20000
$PM_{10}$	dust and ash	2200
N	nutrient enrichment	3480
pesticide	ecotoxicity	270,000
slag	solid waste	120
water effluent	nutrient enrichment	0.8

mental value of HC was calculated to be 20000 RMB/t. However, the characterization factors between NOx and CO on photochemical ozone formation have not been obtained, because the influence of NOx on photochemical ozone formation is highly dependent on the pollutant concentrations and meteorological conditions. Thus the monetary environmental value of NOx, 8000 RMB/t, was taken from ref 57, in which one part of the environmental impact resulted from acidification; the other was from photochemical ozone formation, that was 3800 RMB/t.

**Nutrient Enrichment.** The main source of nutrient enrichment was the N fertilizer considered in this study. According to the previous works,  $^{42,45,50}$  the economic losses of drinking water and fishery caused by the nutrient enrichment of N fertilizer were 114 million RMB from  $61.2\times10^4\,\mathrm{hm^2}$  rice fields. The amount of N fertilizer used was 900 kg/hm² on average, and the loss rate of N fertilizer was 6%, thus the monetary environmental value of the N on the nutrient enrichment effect was estimated to be 3480 RMB/t. On the other hand, water effluent is also one of the pollutant emissions resulting in the nutrient enrichment. The monetary environmental value of water effluent was calculated based on China's pollution charge schedule.

**Dust and Ash.**  $PM_{10}$  is considered as the main pollutant leading to the impact of dust and ash. The direct economic losses of dust and ash have not been evaluated in China; therefore, the monetary environmental value of dust and ash was calculated based on China's pollution charge schedule and the pollution equivalent weight between  $SO_2$  and  $PM_{10}$ . In addition, the value 2200 RMB/t is equivalent with the data in ref 57.

**Ecotoxicity.** The main source of ecotoxicity resulted from the pesticide application in the rice growth process in this paper. Therefore the monetary environmental value of ecotoxicity was evaluated based on the economic losses of rice grain due to biological species decrease. Based on the investigation, <sup>45,61</sup> the amount of pesticide application was 3.0 kg per ton of rice grain, the leakage and runoff losses of the pesticide were 18%, the yield reduction of rice grain was 9.5%, and the scale price of rice grain was 1540RMB/t, so the monetary environmental value of ecotoxicity could be estimated to 27000 RMB per ton of pesticide.

**Solid Waste.** The slag residue of rice straw was considered as the main source of solid waste. The monetary environmental value of solid waste, 120 RMB/t, was taken from ref 57, which was also evaluated based on the pollution charge schedule.

The monetary environmental values of pollutants in China are shown in Table 7.

Table 8. Environmental Cost of Biomethanol in the Life Cycle

		environmental cost of biomethanol (RMB/(t biomethanol))				
impact category	pollutant	rice cultivation	transportation of rice straw	methanol production	methanol consumption	total
global warming (GW)	CO <sub>2</sub>	-152.80	1.07	146.40	73.54	68.21
	$CH_4$	71.74	-	0.39	-	72.13
	NOx	-	0.90	23.76	22.26	46.92
acidification (AC)	$SO_2$	-	-	3.14	-	3.14
	NOx	-	0.15	3.90	3.65	7.70
photochemical ozone formation (PO)	CO	-	0.05	1.12	11.24	12.41
. ,	HC	-	0.08	-	20.87	20.95
	NOx	-	0.13	3.52	3.30	6.96
nutrient enrichment (NE)	N	1.85	-	-	-	1.85
	water effluent	-	-	0.80	-	0.80
ecotoxicity (ET)	pesticide	44.55	-	-	-	44.55
soot and ash (SA)	$PM_{10}$	-	0.01	2.05	0.68	2.74
solid waste (SW)	slag	-	-	49.20	-	49.20
total (RMB/(t biomethanol))		-34.66	2.39	234.28	135.55	337.6

According to the inventory data of biomethanol production in the whole life cycle and the monetary environmental values of the pollutants, the environmental cost of biomethanol can be obtained as

$$PE = \sum_{k=1}^{R} \sum_{i=1}^{N} \sum_{j=1}^{M} W(i,j) \cdot PWR(j,k)$$

where PE is the environmental cost of per ton of biomethanol, W(i,j) is the amount of the j pollutant emissions in the i process, and PWR(j,k) is the monetary environmental value of the k impact category of the j pollutant.

The results of environmental cost of biomethanol in the whole processes are shown in Table 8.

The results show that the total environmental cost is 337.6 RMB per ton of biomethanol. For the different process phase, the methanol production leads to the most serious environmental impact, which accounts for 69.4% of total environmental cost. Thus not only the energy efficiency of biomass conversion is an important performance for producing methanol but also the environmental influences of this phase should be concerned. The second environmental impact is from the biomethanol enduse by automobiles, accounting for about 40.2%, in which the effect of global warming from the greenhouse gas CO<sub>2</sub> makes the most environmental impact in this phase, and the emissions of HC, CO, and NOx bring another important effect of photochemical ozone formation. In the transport of rice straw phase, the environmental cost is 2.39RMB/(t biomethanol) and only occupies less than 1.0%. It can be seen that the transport distance of biomass has little effect on the environment, thus the biomass collection radius is not an important factor for the environmental performance in the life cycle, whereas it has significant influence on the economic performance.<sup>39</sup> On the contrary, the net environmental cost is -34.66 RMB/(t biomethanol) during rice cultivation, that is the environmental load is reduced by 10.3% of the total environmental cost. The results show that the photosynthetic carbon fixation of rice straw growth can make a negative effect on the environment in this phase; therefore, it is favorable for methanol production from biomass to decrease the environmental load.

The comparison of the environmental impact can also be made among the different categories. The contributions of the various environmental impact categories are shown in Figure 3.

From Figure 3 and Table 8, it can be seen that the effect of global warming is the highest of all calculated impact categories, accounting for 55.4% of the total environmental cost. In addition, the greenhouse gas releases mainly in methanol

production and consumption of biomethanol. The reason is that a great amount of carbon dioxide releases from the fuel combustion. However, during the rice growth, the effect of global warming is presented negatively, which is -24% of the total environmental cost, including greenhouse gas  $CO_2$  is fixed by photosynthesis and  $CH_4$  emissions from the rice paddy field. And the environmental cost of  $CO_2$  and  $CH_4$  is respectively -152.8 and 71.7 RMB/(t biomethanol) in this phase, which occupy -81.5% and 38.3% of the net effect of global warming. Thus, on the one hand, the global warming effect could be greatly reduced using biomethanol from the agriculture waste due to the photosynthesis of rice growth; on the other hand, the greenhouse gas  $CH_4$  is also suggested to be taken into account in the rice cultivation because of its obvious influence.

Besides the global warming impact, the influences of photochemical ozone formation, ecotoxicity, and bulk waste are as well as important impact categories. The ecotoxicity impact accounts for 13.2% of the total environment cost due to the pesticide used in the rice growth. The effect of photochemical ozone formation also occupies 12% of the total environment cost. This impact results mainly from the emissions of HC, CO, and NOx during the biomethanol consumption by automobiles, although the effect of photochemical ozone formation from methanol fuel may significantly decrease compared with gasoline fuel. 56 Moreover, the solid waste from the biomass ash also occupies 14.5%, because the biomass ash has not been considered for recycling use in this study. Therefore, the solid waste effect could be greatly decreased by recycling use in the agriculture field. The other impacts, the acidification effect from SO<sub>2</sub> and NO<sub>3</sub>, is rather small, only accounting for 3.2%, because the S and N content of biomass is much less than that of coal. The effects of nutrient enrichment and soot and ash are less

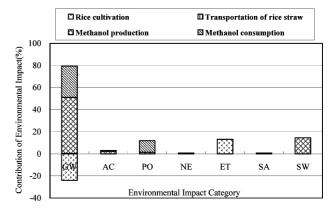


Figure 3. Contributions of different environmental impact categories.

than 1%, which could be nearly neglected in this life cycle of biomethanol.

Considering that the economic cost is an internal cost and the environmental cost is an external cost, the real cost of biomethanol product will be the sum of the economic and environmental cost. The real cost of biomethanol could be achieved 2685 RMB/(t biomethanol). It can be found that the environmental cost accounts for 12.6% of the biomethanol real cost. Therefore, it is beneficial for the methanol production from biomass to the environment impact, and the economic performance may be a more important factor for the future commercial application of biomethanol in China.

#### 5. Conclusions

In this study, the integrated analysis on energy, economic, and environmental performance of biomethanol is performed. Several conclusions are drawn as follows:

- (1) From the analysis of thermodynamic performance, the methanol yield can reach 0.308 kg/(kg rice straw), that is, the energy efficiency of rice straw conversation to biomethanol is 42.7% based on the suggested methanol production process in this study.
- (2) The economic cost of the biomethanol product is evaluated to be 2347 RMB/t, in which the raw material cost is the dominating cost factor, and the unit investment cost is another important factor. While the coal price is higher than 750 RMB/t, the economic performance of biomethanol will be better than that of coal-based methanol in China, although the investment cost of the biomethanol system is higher. Therefore biomethanol will be becoming more competitive when the shortage of fossil fuel is more serious in the future.
- (3) Based on the method of LCA, the environmental cost of biomethanol is obtained, which is about 337.6 RMB per ton of biomethanol. In the whole life cycle, the main pollutant emissions are from the biomethanol production process and biomethanol end-use by automobiles, and global warming is the most influential factor of the discussed impact categories. However, CO<sub>2</sub> is fixed due to photosynthesis in the growth of rice, thus the effect of global warming can be significantly reduced by biomass utilization compared with coal-based methanol.
- (4) Combining the economic cost with the environmental cost, the real cost of biomethanol can be achieved 2685 RMB/(t biomethanol) in this paper. From the integrated performance of the biomethanol production process, the rice straw as raw material of producing methanol is beneficial to both utilization of agriculture waste and improvement in the environment. Therefore agriculture straw will be an environmentally friendly substitute for producing automobile fuel.

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