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Wood Waste Steam Gasification to Methane-Enriched Fuel Gas

Boris N. Kuznetsov^{*a,b} and Maxim L. Shchipko^a

^a *Institute of Chemistry and Chemical Technology SB RAS, Akademgorodok, Krasnoyarsk, 660036 Russia*

^b *Siberian Federal University, 79 Svobodny, Krasnoyarsk, 660041 Russia*¹

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The influence of catalytically active in methanization reaction slag materials on the yield and composition of gaseous products obtained by steam gasification of wood sawdust in a reactor with fluidized bed was studied. It was found that cheap catalyst on basis of Martin slag allows to produce from wood waste the methane-enriched gas. Its calorific value is on 30 % higher in comparison with the traditional steam gasification process. The part of potential heat of the initial raw material, transforming to heat of the produced gas is increased by 10 relative %.

Key words: wood sawdust, steam gasification, modified Marting slag, fluidized bed, methane-enriched gas.

Introduction

In the traditional autothermal gasification processes near 30 % of the initial solid fuel exposes to combustion in order to compensate the endothermic reactions of carbon with water steam and carbon dioxide and to maintain the required temperature of the process. The optimal level of temperature should supply the acceptable intensity of the chemical and diffusion stages of gasification process [1].

Elevated temperatures increase the solid fuel consumption for burning process. Besides, at the same composition of gasification agent, the growth of temperature leads to increase in produced gas the concentration of carbon monoxide and to simultaneous decrease of hydrogen amount. It should be note that low

ratio H_2/CO is not favorable to use this gas for syntheses of chemicals and liquid fuels.

The application of catalysts in gasification processes allows to reduce the temperature without decreasing of process intensity. For steam gasification of carbon such catalysts as hydroxides, carbonates, chlorides, sulfates of alkaline and alkaline-earth elements, metals of VII group, alloy materials etc are used. Most-known catalysts are potassium and sodium carbonates.

Above mentioned catalysts can be used also for carbon gasification by CO_2 . As a rule, the catalysts are supported on solid fuel by impregnation method. The processes of catalytic gasification are carried out at temperature range 490-570 °C.

* Corresponding author E-mail address: bnk@icct.ru

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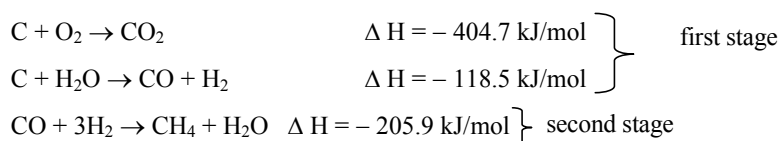
Along with the increase the rate of carbon gasification the catalyst can accelerate the other reactions in gas phase. This makes possible to regulate the composition of produces syn-gas and to compensate the endothermic effects of carbon reaction with water-steam at the expense of acceleration of methanization and CO-shift reactions [2-9].

Mainly the two-stage processes of solid biomass gasification to methane are used. At first stage a syn-gas (mixture of hydrogen and carbon monoxide) is produced. The second stage includes the catalytic conversion of syn-gas to methane [10-13].

The known one-stage process (Hoffman process) has been developed for methane production [14]. This process is based on the solid fuel gasification by water steam in the presence of alkali or nickel catalyst. Since the methanization reaction is exothermic it makes possible to supply by heat the gasification process without the use of molecular oxygen. In the majority of cases the modern gasification technologies use oxygen for the combustion of some part of solid fuel.

Differences in the one stage and two-stage processes of methane production through gasification of carbon-containing raw material illustrate the following chemical equations.

Two-stage process:



One-stage process:



One-stage process has the following advantages: more simple technological scheme, lower number of apparatus, no demands in oxygen. But some objective reasons did not

allow to find the acceptable technological solutions for the realization of one-stage gasification of solid fuel to methane. The most important problem is the difference in optimal temperature ranges for methanization reactions (200-400 °C) and gasification reactions (more 800 °C). In the case of biomass gasification the use of catalysts is restricted by their fast deactivation, owing to intensive coking of the catalyst with tar products of biomass thermal decomposition.

The goal of the present study was the development of one-stage process of waste-wood gasification to gaseous products with a high content of methane. In order to achieve this object the problems of optimal design of the process technology and the selection of cheap and available catalysts were solved.

Experimental

Schematic diagram of gasification installation, based on the original patent [15] is given on Fig. 1. The gasification experiments included the following steps. Wood sawdust (fraction ≤ 2 mm) dried to moisture content ≤ 18 % wt. were download into feeder (1). Reactor (2) and fluidized catalyst bed (3) are heating by burner working on diesel fuel (did not shown

on the scheme). After reaching the temperature of catalyst bed 500-600 °C the supply of diesel fuel is break off and the feeding of wood sawdust and water steam is started. The steam has the

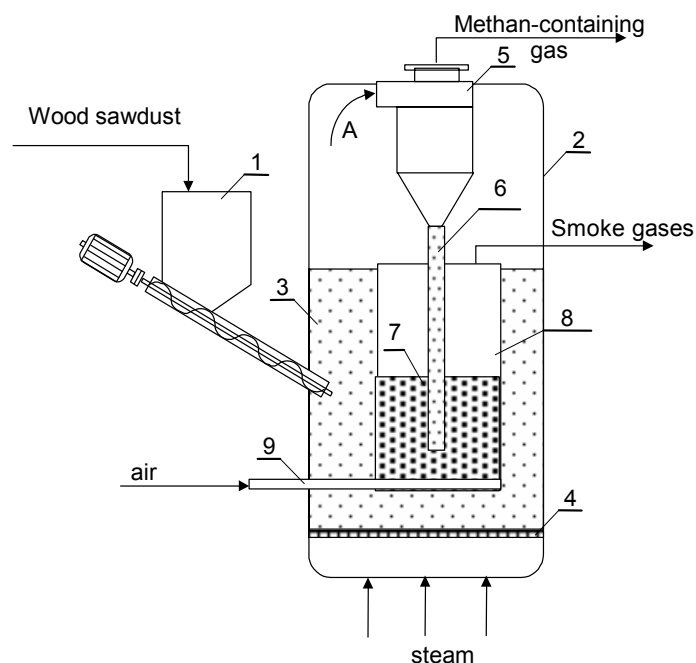


Fig.1. Schematic diagram of installation for biomass gasification in fluidized bed of methanization catalyst. 1 – feeder, 2 – reactor, 3 – fluidized bed of catalyst, 4 – gas distribution grid, 5 – build-up cyclone, 6 – pipe for char product, 7 – fluidized bed of char product, 8 – combustion chamber, 9 – injector for air supply

temperature 420°C which corresponds to standard characteristics of steam using in energetics.

Raw material particles feeding to heated fluidized bed of catalyst expose to thermal destruction with the formation of volatile and solid char products. The char product yield varies between 30-35 % relative to mass of dry raw material. Some part of this char reacts with a water steam. The another part of a char undergoes powdering to particles with sizes less 0.5 mm which transfer by the air flow to cyclone (5). On Fig. 1 the direction of char particles flow is shown by indication arrow “A”. Solid char particles separated from gas flow in cyclone (5) move through pipe (6) to combustion chamber (8), where they are burned in a medium of down-blown air. The produced heat goes to gasification zone (3) through the wall of a combustion chamber (8) and the smoke gases are removed from a chamber without mixing with a produced methane-containing gas.

The heat for gasification process is collected from three main sources including overheated water-steam, methanization reactor with fluidized bed of catalyst and combustion chamber. The measurements of a heat transfer rates show that the last source of heat is no more than 25 % from a total heat obtained by char product combustion. The significant part of a heat is lost with smoke gases. Thus, it is reasonable to use the smoke gases for production of the overheated water-steam.

The selection of catalytically active materials for fluidized bed was made taking into account the extreme conditions of their work in studied gasification process. Therefore, the different slag materials of metallurgy industry having the high mechanical resistance and thermal stability [16] were tested in methanization of the mixture $\text{CO} + \text{H}_2 + \text{H}_2\text{O}$. For the comparison the synthetic methanization catalyst ANKM-1E, produced by “Angarsk plant of catalysts and organic synthesis”

was used. This catalyst (corresponds TU 2178-036-47317879-97) contains 34-38 % wt. NiO and near 48 % Al_2O_3 after calcinations at 800 °C.

Catalytic activity of samples was studied in a quartz reactor with diameter 25 mm at temperature 450 °C. The mixture of syn-gas and water-steam ($\text{CO} - 2.5$ % vol., $\text{H}_2 - 12.0$ % vol., rest – H_2O) was blown through the bed of catalyst.

Catalytic activity in methanization process was estimated on basis of methane concentration in dry gas on the reactor exit. Concentration of methane produced with the use of industrial catalyst ANKM-1E was taken as 100 %.

Wear resistance of the studied materials was evaluated with the use of steel cylinder with inner diameter 25 mm and high 310 mm. Solid material was grinded up to particles with sizes 0.5-3.0 mm. The sample of grinded material (50 cm^3) was weight and charged to cylinder along with 5 steel balls with diameter 15.08 mm. Cylinder was rotated with speed 25 revolutions per minute during 40 min. After that the material was separated on the sieve with holes 0.5 mm. Material particles with higher sizes were put back to cylinder for the next treatment procedure. The

wear resistance value was estimated as the time of 50 % destruction of the initial sample.

The abrasivity was evaluated on basis of the decrease of mass of steel cylinders after rotating in steel drum together with 200 cm^3 of studied material. Diameter of drum is 18 cm, high 17 cm, rate of rotating 18.5 revolutions per minute, time of treatment 4 hours. Used cylinders from steel 12X18H10T have diameter 12 mm and length 24 mm. The abrasivity value was estimated as ratio of the decrease of mass of cylinders treated with studied material and with grinded chamotte.

Results and discussion

Data obtained for the most active metallurgical slags are shown on Fig. 2. It was found that at the used condition of methanization, the Martin slag after the special activation treatment (sample 5) shows the high catalytic activity which reaches 40 % from activity of industrial catalyst. The degree of steam conversions was varied between 20-60 %.

The most pronounced effect of catalytically active material can be achieved by means of increase the time of contact between gaseous reagents and catalyst, for instance at the expense

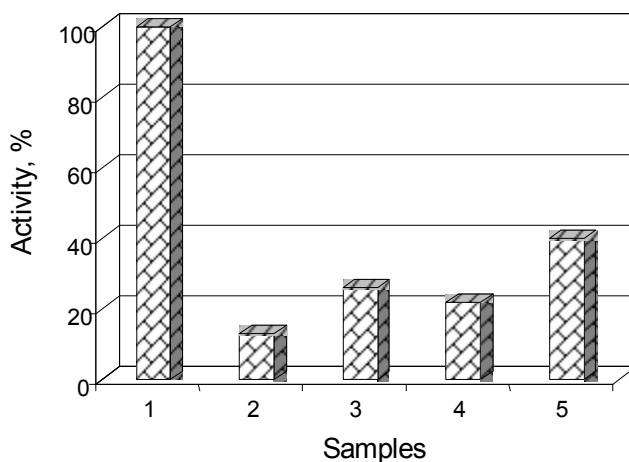


Fig. 2. Catalytic activity of metallurgical slag materials in reaction of methanization of the mixture $\text{CO} + \text{H}_2 + \text{H}_2\text{O}$. 1 – catalyst ANKM-1E, 2 – converter slag, 3 – steel-smelting slag, 4 – Martin slag, 5 – activated Martin slag

of the high of fluidized bed in gasification reactor. But this technical solution can be fulfilled only on the bigger gasifier since it is well known [17] that the high of fluidized bed should be less or equal to one and half of its diameter.

Since the application of rather cheap metallurgical slag instead of synthetic industrial catalyst looks attractive from economical point of view, there is reason for concern that the stability of slag composition and properties is not ensured.

Therefore, it is of a practical interest to obtain data about stability of slag characteristics during long time period. For the use in gasifier with fluidized bed the catalytically active slag material should possess such properties as mechanical and thermal resistance, low abrasivity, availability and stable characteristics.

Tables 1 and 2 demonstrate the variation with time some characteristics of Martin and converter slags. Time between sampling was 6-8 months. Therefore, the experimental data cover

Table 1. Some characteristics of slag materials

| Characteristics | Martin slag | | | | | Converter slag | | | | |
|--------------------------------|--------------------|------|------|------|------|----------------|------|------|------|------|
| | Symbols of samples | | | | | | | | | |
| | M1 | M2 | M3 | M4 | M5 | K1 | K2 | K3 | K4 | K5 |
| Abrasivity, % | 5.5 | 5.5 | 5.4 | 5.7 | 5.6 | 4.2 | 4.0 | 4.2 | 4.1 | 4.0 |
| Half-period of destruction, h | 17.5 | 15.0 | 17.0 | 16.5 | 16.5 | 7.0 | 7.5 | 9.0 | 7.5 | 8.2 |
| Composition, % mas.: | | | | | | | | | | |
| SiO ₂ | 24.6 | 21.5 | 19.9 | 19.4 | 22.1 | 17.4 | 11.7 | 14.6 | 14.6 | 15.0 |
| Al ₂ O ₃ | 9.4 | 7.6 | 10.2 | 6.9 | 8.5 | 2.2 | 1.0 | 2.6 | 3.8 | 2.4 |
| CuO | 39.4 | 37.6 | 42.3 | 38.6 | 37.3 | 44.5 | 47.0 | 44.9 | 44.9 | 45.3 |
| MgO | 13.5 | 12.0 | 9.4 | 14.2 | 11.6 | 6.3 | 5.2 | 4.3 | 4.1 | 4.7 |
| FeO | 6.1 | 9.2 | 8.6 | 8.6 | 10.4 | 19.6 | 21.6 | 20.1 | 17.3 | 18.0 |
| Cr ₂ O ₃ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.8 | 2.4 | 0.9 | 0.6 | 0.1 |

Table 2. Statistical indicators of slags homogeneity

| Characteristics | Mean value | | Variance | | Standart deviation | |
|--------------------------------|-------------|----------------|-------------|----------------|--------------------|----------------|
| | Martin slag | Convertor slag | Martin slag | Convertor slag | Martin slag | Convertor slag |
| Abrasivity, % | 5.54 | 4.10 | 0.01 | 0.01 | 0.09 | 0.08 |
| Half-period of destruction, h | 16.5 | 7.8 | 0.70 | 0.48 | 0.76 | 0.63 |
| Composition, % mas.: | | | | | | |
| SiO ₂ | 21.50 | 14.66 | 3.39 | 3.28 | 1.68 | 1.65 |
| Al ₂ O ₃ | 8.52 | 2.40 | 1.41 | 0.80 | 1.09 | 0.82 |
| CuO | 39.04 | 44.72 | 3.21 | 2.71 | 1.63 | 1.50 |
| MgO | 12.14 | 4.92 | 2.78 | 0.62 | 1.52 | 0.72 |
| FeO | 8.58 | 19.32 | 1.97 | 2.34 | 1.28 | 1.40 |
| Cr ₂ O ₃ | 0.00 | 1.36 | - | 1.11 | - | 0.96 |

Table 3. Influence of conditions of wood sawdust gasification on the yield and composition of produced gases

| Indices | Birch sawdust in bed of quartz sand | Birch sawdust in bed of activated Martin slag | Aspen sawdust in bed of activated Martin slag |
|---|-------------------------------------|---|---|
| Steam consumption (420°C) kg/kg sawdust | 1.7 | 1.2 | 1.2 |
| Temperature in the upper bed of slag, °C | 650 | 655 | 660 |
| Yield of dry gas, m ³ /kg sawdust | 0.68 | 0.58 | 0.60 |
| Composition of dry gas, % mas.: | | | |
| H ₂ | 22.3 | 17.9 | 16.4 |
| CO | 5.8 | 1.2 | 1.9 |
| CH ₄ | 27.8 | 42.8 | 41.3 |
| C _n H _m | 2.1 | 2.4 | 1.9 |
| CO ₂ | 39.6 | 34.5 | 33.8 |
| N ₂ | 2.4 | 1.2 | 4.7 |
| Heat of combustion of dry gas, kJ/nm ³ | 14150 | 18600 | 17800 |

Table 4. Biomass air-steam gasification processes performance

| Type of gasifier | Fixed-bed | | Fluidized bed | |
|---|---|---|---------------|---------------------|
| Technology name | FBG-50 | FBG-60 | “Milena” | ICCT SB RAS |
| Fuel nature | Wood chips sawdust Pellets Corncob | Husk of rice, buckwheat, oat, stems, etc. | Waste-wood | Table 3 |
| Fuel size, mm | 10-50 (wood chips) 0.5-2.0 (sawdust) | Diameter 2-3, length 2-20 | 5-40 | 0.5-5.0 |
| Fuel moisture, % | Up to 20 (wood chips) Up to 10 (sawdust) | Up to 10 | Up to 30 | Up to 20 |
| Feeding | Hand feed | Hand feed | Screw feeder | Pneumatic transport |
| Process intensity*, MW _h /m ² | 1,45 | 1,56 | 3,20 | 2,70 |
| Temperature of gas, °C | 250-400 (after gasifier) | 250-400 | 800-950 | 640-680 |
| Heat of combustion, MJ/nm ³ | 4.5-5.5 | 4.1-4.8 | 9.5-10.5 | 17.8-18.6 |

$$* \text{Process intensity (MW}_h/\text{m}^2) = \frac{\text{Gas productivity (nm}^3/\text{c)} \times \text{Heat of combustion (MJ/nm}^3)}{\text{Inner cross - section of gasifier (m}^2)}$$

the period of time more than 3 years. Obtained results show that studied slag materials have rather stable characteristic during long time and they can be used as cheap gasification catalysts in fluidized bed reactors.

Experiments with wood-sawdust gasification were carried out with Martin slag (fraction 0.5-1.0 mm). The catalytically inert quartz sand was used for a comparison. Birch

and aspen sawdust were used as an initial raw material. Experimental data illustrated the influence of sawdust gasification conditions on the yield and composition of produced gases are given in the Table 3.

Obtained results show that the use of fluidized bed of Martin slag, which is active in reactions of carbon oxides hydrogenation to methane, increases considerably the

concentration of methane in gas produced from wood sawdust.

In the comparison with sawdust gasification in the fluidized bed of inert material – quartz sand the observed growth of methane concentration was 48-54 relative %. At the same time some reduction in the volume of produced methane-containing gas (on 12-15 relative %) and simultaneous increase of a heat of gas combustion (on 30 relative %) were detected. Obviously, the both of these facts can be interpreted by intensification of reactions of carbon oxides hydrogenation to methane in the presence of Martin slag catalyst. It should be noted that the part of potential heat of wood biomass converting to the potential heat of produced gas was increased by 10 relative % in the presence of catalyst.

The temperature in gasification reactor is defined by a thermal balance of the gasification process which is regulated by heated steam flow. The reduction of a steam consumption in the presence of catalyst, probably stipulated by an extra heat producing by methanization reactions.

Table 4 shows the biomass air-steam gasification processes performance. Developed gasification process is compared with industrial gasifiers “Flex Technologies, Inc.” [18] and with Dutch pilot installation with fluidized bed [19].

At present the number of commercial fixed-bed gasifiers with productivity near 5 MW_n is approaching to few hundreds. But gasifiers with fluidized bed, despite on their

higher intensity (Table 4) are presented only by pilot and semi-industrial plants. Obviously, this fact is connected with lower capital costs of fixed-bed gasifiers [20].

For the compared processes the difference in calorific value of produced gases is conditioned mainly by presence of N₂. In the process under development (Table 3) N₂ concentration in fuel gas is less 5 %, thanks to the special design of gasifier. In other gasification processes the amount of N₂ varies from 50 to 70 % [19, 20] as a result of mixing the fuel and smoke gases.

It is worth to note that the intensity of gasification processes in reactors with fluidized bed is higher as compared to fixed-bed gasifiers. In the comparison with “Millena” gasifier the process under development operates at lower (on 200 °C) gasification temperature.

In whole, the obtained results allow to make a conclusion that the level of catalytic activity of specially treated Martin slag provides the increased concentration of methane in the process of wood sawdust gasification by steam. The developed gasification process makes it possible to produce from waste wood the methane-containing gas with calorific value on 30 % higher in comparison with the traditional steam gasification process. Besides, the part of potential heat of the initial raw material, transforming to the potential heat of the produced gas was increased by 10 relative %.

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Газификация древесных отходов в обогащенный метаном топливный газ

Б.Н. Кузнецов^{а,б}, М.Л. Щипко^а

^а *Институт химии и химической технологии СО РАН,
Россия 660049, Красноярск, ул. К. Маркса, 42*

^б *Сибирский федеральный университет,
Россия 660041, Красноярск, пр. Свободный, 79*

Изучено влияние рудных материалов, каталитически активных в реакции метанирования, на выход и состав газообразных продуктов, полученных паровой газификацией древесных опилок в реакторе с псевдооживленным слоем. Установлено, что применение дешевого катализатора на основе мартеновского шлака позволяет получать из древесных отходов обогащенный метаном газ. Теплота его сгорания на 30 % выше по сравнению с традиционным процессом паровой газификации. Доля потенциального тепла исходного сырья, перешедшая в тепло продуцируемого газа, возрастает на 10 % относительных.

Ключевые слова: древесные опилки, паровая газификация, модифицированный мартеновский шлак, псевдооживленный слой, обогащенный метаном газ.
