Development of Nature Protection Technologies of Hydrocarbon Wastes Disposal on the Basis of High-Temperature Pyrolysis

To cite this article: V D Shantarina et al 2016 IOP Conf. Ser.: Mater. Sci. Eng. 154 012016

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Development of Nature Protection Technologies of Hydrocarbon Wastes Disposal on the Basis of High-Temperature Pyrolysis

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Abstract. The research shows the thermal balance of low-temperature pyrolysis of birch sawdust with the possibility of further development of nature protection technology of hydrocarbon wastes disposal with secondary useful products production. The actual problem was solved by preventing environmental pollution by greenhouse gases using pyrolysis process as a method of disposal of hydrocarbon wastes with secondary useful products production. The objective of paper is to study features of the processes of thermal processing of wastes and development of environmentally sound technology of disposal C-containing wastes, contributing to the implementation of the pollution prevention concept.

1. Introduction

For the preservation and development of civilization it is necessary to move to the noosphere - the sphere of mind (V I Vernadsky). The future of the planet hangs by a thread and, to prevent this, humankind has decided to establish firm control over emissions into the atmosphere of six greenhouse gases: carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, sulfur hexafluoride (the Kyoto Protocol, 1997).

Environmental problems have excited the world community long time ago. In 1992, the United Nations Framework Convention on Climate Change was adopted by 185 states in order to unite efforts to prevent dangerous climate change and contribute to the stabilization of greenhouse gases i.e. provide a low-carbon development path.

On January 24 in Davos, UN Secretary General Ban Ki-moon spoke at the plenary session of the World Economic Forum, dedicated to the fight against climate change and promoting sustainable development and economic growth (Published on 01/24/2015). He stated that 2015 should become the year of global actions. Ban Ki-moon appealed of achievement a low-carbon economic development in order to counter the threats of global warming. Unfortunately, this is a long way of development and at the moment, development of civilization is impossible without carbon.

In 1972 in Stockholm (Sweden), the UN environmental conference, relating to the relationship between economic development and degradation of the environment, was held for the first time. After the Conference, the Government established the United Nations Environment Program (UNEP), which remains the leading institution in the world on environmental issues.

On 3-14 June, 1992 in Rio de Janeiro (Brazil, Rio-20) was held the UN Conference on Environment and Development. At the meeting, a declaration was adopted, which stated that "for achieving sustainable development, environmental protection shall constitute an integral part of the development process and it cannot be considered in isolation from it." The declaration includes 27 principles that define the rights and obligations of countries to ensure the development and welfare of the people. At a conference in Rio de Janeiro, «Agenda 21» was adopted - a program of how to make development sustainable from a social, economic and environmental points of view.

Recently, the 21st UN Conference on Climate Change was held. It ended in December 2015 in Paris with the adoption of a new agreement. In the negotiations participated 195 countries and have set

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emission reduction commitments, taking into account all the challenges and opportunities. In the negotiations, 195 countries participated that set emission reduction commitments, taking into account all the challenges and opportunities.

Development of nature protection technology of hydrocarbon wastes disposal with producing secondary useful products is an urgent task of preventing environmental pollution, using the pyrolysis process as a method of disposal hydrocarbon wastes with producing secondary useful products, contributing to the implementation of the concept of pollution prevention.

2. Models and methods

The amount of heat, generated by the complete combustion of the entire mass of generated organic product in the liquid phase [1-3] (resin, acetic acid, methanol, etc.).

\[ Q(T^w) = Q(C)_{pyr} + Q(C, H, O, Ne)_{pyr} - Q(H_2O) + Q(GG) + Q_p. \]  

where \( Q(C)_{pyr} \) is the amount of heat released by full combustion of the entire mass of the resulting charcoal, kJ;

\( Q(C, H, O, Ne)_{pyr} \) is amount of heat released by complete combustion of the entire mass of generated organic product as a liquid phase (resin, acetic acid, methanol, etc.), kJ;

\( Q(H_2O) \) - the amount of heat absorbed by evaporation of moisture from the fuel and resulting "chemical" water, kJ;

\( Q(GG) \) - the amount of heat released by full combustion of the entire mass of the resulting combustible gas, kJ;

\( Q_p \) - the amount of heat generated in the pyrolysis of the entire mass of wood fuel, kJ.

The calorific value of wood fuel, calculated using the formula of Mendeleyev:

\[ Q(T^w)_{m} = 4.19(8100\phi(C)_r + 24600\phi(H)_r - 600\cdot W^p) = 18647.55\,kJ \, / \, kg. \]  

The lowest working calorific value of generated combustible gas:

\[ Q(GG)_{m} = 4.19(2580 \cdot \mu(H_2)^G \oplus 3045 \cdot \mu(CO)^G + 8517 \cdot \mu(CH_4)^G) = 7650.5\,kJ \, / \, kg. \]  

Let us assume the lowest calorific value of liquid phase to be:

\[ Q(C, H, O, Ne, m)_{m} = 32500\,kJ \, / \, kg. \]  

Assume the calorific value of the charcoal as following:

\[ Q(C)_{p} = 34000\,kJ \, / \, kg. \]  

The amount of heat generated during the pyrolysis of wood:

\[ Q_p = Q(T^w)_{w} - Q(C)_{wp} - Q(C, H, O, Ne, m) - Q(GG)_{w} = m(T^w_p)_{m} - m(C)_{wp}Q(C)_{m} - m(C, H, O, Ne, m)Q(C, H, O, Ne)_{m} - V(GG)^GQ(GG)_{m} = 0.050 \cdot 18647.55 - 0.0147 \cdot 34000 - 0.0123 \cdot 32500 - 0.004 \cdot 7650.5 = 2.2\,kJ, \] 

where \( Q(T^w)_{w} \) - the amount of heat released by the complete combustion of the entire mass of fuel wood, taken for pyrolysis, kJ.

According to the developed model, let us consider how is the calorific value of generated combustible gas changing, depending on the wood pyrolysis temperature. It is known that in the processes of gasification of wood fuel in the gas generator with the inverse process of combustion, wood resin and organic products are not formed, since the temperature 700-750°C, because they are almost entirely gasified to generator gas. Then, the ratio of fullness of fuel carbon gasification will be equal to:
\[ \zeta^* (C)^G = 1 - \varphi (C)^G \text{pr} = 1 - 0.63 = 0.37. \] (7)

Mass of gasified carbon fuel is:
\[ m^* (C)^G_T = \frac{m^* (C)^G_T \cdot \zeta^* (C)^G}{\zeta(C)^G} = \frac{0.0043 \cdot 0.37}{0.09} = 0.177kJ. \] (8)

Mass of generated carbon dioxide in combustion gas is equal to:
\[ m^* (CO)^G_T = \frac{m^* (CO)^G_T - \varphi (C)^G}{m^* (CO)^G_T} = 0.177 = 0.0159kg. \] (9)

Mass of generated carbon monoxide in the combustion gas is equal to:
\[ m^* (CO)^G_T = \frac{m^* (CO)^G_T - \varphi (C)^G}{m^* (CO)^G_T} = 0.0059 \cdot 12 = 0.0025kJ. \] (10)

Mass of carbon fuel spent on generation of carbon dioxide is equal to:
\[ m^* (CO)^G_T = \frac{m^* (CO)^G_T - \varphi (C)^G}{m^* (CO)^G_T} = 0.0059 \cdot 12 = 0.0025kJ. \] (11)

Mass of carbon fuel spent on methane gas generation:
\[ m^* (CH_4)^G_T = \frac{m^* (CH_4)^G_T - \varphi (C)^G}{M(CH_4)} = 0.0013 \cdot 16 = 0.0017kJ. \] (12)

The amount of kilomoles of generated nitrogen gas (N2) as a part of the fuel gas:
\[ n^* (N_2)^G_T = \frac{m^* (N_2)^G_T}{M(N_2)} = \frac{0.00003}{28} = 10^{-6} \text{ kmole}. \] (13)

The number of kilomoles of generated carbon dioxide as a part of combustible gas:
\[ n^* (CO)^G_T = \frac{m^* (CO)^G_T}{M(CO)} = \frac{0.0177}{44} = 0.0004 \text{ kmole}. \] (14)

The number of kilomoles of generated carbon monoxide as a part of combustible gas:
\[ n^* (CO)^G_T = \frac{m^* (CO)^G_T}{M(CO)} = \frac{0.0059}{28} = 0.0002 \text{ kmole}. \] (15)

The number of kilomoles of generated methane gas as a part of combustible gas:
\[ n^* (CH_4)^G_T = \frac{m^* (CH_4)^G_T}{M(CH_4)} = \frac{0.0017}{16} = 0.0001 \text{ kmole}. \] (16)

The number of kilomoles of generated combustible gas in terms of the absolutely dry one:
\[ n^* (GT)^G_T = n^* (N_2)^G_T + n^* (CO)^G_T + n^* (CO)^G_T + n^* (CH_4)^G_T = 10^{-6} + 0.00004 + 0.0002 + 0.0001 = 0.0007 \text{ kmole}. \] (17)

Mass of generating combustible gas:
\[ m^* (GG)^G_T = m^* (CO)^G_T + m^* (CO)^G_T + m^* (N_2)^G_T + m^* (CH_4)^G_T = 0.253kJ. \] (18)

The amount of generated gas at the initial conditions:
\[ V^* (GG)^G = 22.4 \cdot n^* (GG)^G 22.4 \cdot 0.0157m^3. \] (19)

Density of absolutely dry combustible gas:
\[ \rho \ast (GG)^G = \frac{m \ast (GG)^G}{V \ast (GG)^G} = \frac{0.0253}{0.0157} = 1.6115 \text{kg/m}^3 \]  

The mole fraction of gases CO2, CO, CH4, N2 in the combustion gas:

\[ \mu \ast (CO_2)^G = \frac{n \ast (CO_2)^G}{n \ast (GG)^G} = \frac{0.0004}{0.0007} = 0.571; \]  

\[ \mu \ast (CO)^G = \frac{n \ast (CO)^G}{n \ast (GG)^G} = \frac{0.0002}{0.0007} = 0.286; \]  

\[ \mu \ast (CH_4)^G = \frac{n \ast (CH_4)^G}{n \ast (GG)^G} = \frac{0.0001}{0.0007} = 0.143; \]  

\[ \mu \ast (N_2)^G = \frac{n \ast (N_2)^G}{n \ast (GG)^G} = \frac{10^{-6}}{0.0007} = 0.001. \]  

The lowest working calorific value of the gas:

\[ Q \ast (GG)^P = 4.19(2580 \cdot \mu(H_2)^G + 3045 \cdot \mu(CO)^G + 8517 \cdot \mu(CH_4)^G) = 8752.1 \text{kJ/m}^3. \]  

Specific lowest working calorific value of gas:

\[ Q_{sp} \ast (GG)^P = \frac{Q \ast (GG)^P}{\rho \ast (GG)^G} = \frac{8752.1}{1.6115} = 5431.0 \text{kJ/kg}. \]  

Let us consider the pyrolysis process at a temperature of +1000 °C, at which the reaction of water gas begins to flow, i.e. the interaction of carbon fuel with water vapor:

\[ C_{(solid)} + H_2O_{(vap)} \rightarrow CO_{(g)} + H_2(g). \]  

Then the mass of carbon fuel spent on the reaction of water gas, is equal to:

\[ m'(C)^{WG} = \frac{m(H_2O)^{pr} \cdot A(C)}{M(H_2O)} = \frac{0.0164 \cdot 12}{18} = 0.0109 \text{kg}. \]  

Mass of ungasified fuel carbon:

\[ m(C)^{pr} = m(C)^G - m(C)^{WG} = 0.0233 - 0.0086 - 0.0109 = 0.0038 \text{kJ}. \]  

Mass of generated carbon monoxide and hydrogen gas by a water gas reaction:

\[ m'(CO)^{WG} = \frac{m'(C)^{WG} \cdot M(CO)}{A(C)} = \frac{0.0109 \cdot 28}{12} = 0.0254 \text{kg}; \]  

\[ m'(H_2)^{WG} = \frac{m'(C)^{WG} \cdot M(H_2)}{A(C)} = \frac{0.0109 \cdot 2}{12} = 0.0018 \text{kg}. \]  

Mass of generating hydrogen gas as a part of combustible gas:

\[ \dot{m}(H_2)^G = m'(H_2)^{WG} = 0.0018 \text{kg}. \]  

Mass of generating nitrogen gas as a part of combustible gas:

\[ \dot{m}(N_2)^G = m(N_2)^F = 0.00003 \text{kg}. \]  

Mass of generated carbon monoxide as a part of combustible gas:

\[ \dot{m}(CO)^G = m*(CO)^G + m'(CO)^{WG} = 0.0059 + 0.0254 = 0.0313 \text{kJ}. \]  

Mass of generated methane gas as a part of combustible gas:

\[ \dot{m}(CH_4)^G = m*(CH_4)^G = 0.0017 \text{kg}. \]  

Mass of generated carbon dioxide as a part of combustible gas:

\[ \dot{m}(CO_2)^G = m*(CO_2)^G = 0.0177 \text{kg}. \]  

Mass of generated combustible gas:
\document{Transport and Storage of Hydrocarbons
IOP Publishing
IOP Conf. Series: Materials Science and Engineering 154 (2016) 012016 doi:10.1088/1757-899X/154/1/012016

\begin{align}
m(GG) &= m(T)_w - m(C)_{pyr} - m(Z)_r = 0.05 - 0.0038 - 0.0005 = 0.0457 \text{kg} \quad . 
\end{align}

The number of kilomoles of generated hydrogen as a part of the combustible gas:
\begin{align}
\dot{n}(H_2)^G &= \frac{\dot{m}(H_2)^G}{M(H_2)} = \frac{0.0018}{2} = 0.0009 \text{k mole} \quad . 
\end{align}

The number of kilomoles of generated nitrogen gas as a part of the combustible gas:
\begin{align}
\dot{n}(N_2)^G &= \frac{\dot{m}(N_2)^G}{M(N_2)} = \frac{0.00003}{28} = 10^{-6} \text{k mole} \quad . 
\end{align}

The number of kilomoles of generated carbon monoxide as a part of the combustible gas:
\begin{align}
\dot{n}(CO)^G &= \frac{\dot{m}(CO)^G}{M(CO)} = \frac{0.0313}{28} = 0.0011 \text{k mole} \quad .
\end{align}

The number of kilomoles of generated carbon dioxide as a part of the combustible gas:
\begin{align}
\dot{n}(CO_2)^G &= \frac{\dot{m}(CO_2)^G}{M(CO_2)} = \frac{0.0177}{44} = 0.0004 \text{k mole} \quad .
\end{align}

The number of kilomoles of generated fuel gas in terms of the absolutely dry:
\begin{align}
\dot{n}(GT)^G &= \dot{n}(H_2)^G + \dot{n}(N_2)^G + \dot{n}(CO)^G + \dot{n}(CO_2)^G = 0.0025 \text{k mole} 
\end{align}

The amount of generated combustible gas under normal conditions:
\begin{align}
V(GT) &= 22.4 \cdot \dot{n}(GT)^G = 22.4 \cdot 0.0025 = 0.0560 m^3 \quad .
\end{align}

The density of generated gas:
\begin{align}
\dot{\rho}(GG) &= \frac{\dot{n}(GG)}{V(GG)} = \frac{0.0457}{0.0560} = 0.8160 \text{kg/m}^3 \quad .
\end{align}

The mole fractions of gases H2, N2, CO, CH4, CO2
\begin{align}
\dot{\mu}(H_2)^G &= \frac{\dot{n}(H_2)^G}{\dot{n}(GG)^G} = \frac{0.0009}{0.0025} = 0.3600 \quad ; \quad (46)
\end{align}

\begin{align}
\dot{\mu}(N_2)^G &= \frac{\dot{n}(N_2)^G}{\dot{n}(GG)^G} = \frac{10^{-6}}{0.0025} = 0.0004 \quad ; \quad (47)
\end{align}

\begin{align}
\dot{\mu}(CO)^G &= \frac{\dot{n}(CO)^G}{\dot{n}(GG)^G} = \frac{0.0011}{0.0025} = 0.4400 \quad ; \quad (48)
\end{align}

\begin{align}
\dot{\mu}(CO_2)^G &= \frac{\dot{n}(CO_2)^G}{\dot{n}(GG)^G} = \frac{0.0004}{0.0025} = 0.1600 \quad ; \quad (49)
\end{align}

\begin{align}
\dot{\mu}(CH_4)^G &= \frac{\dot{n}(CH_4)^G}{\dot{n}(GG)^G} = \frac{0.0001}{0.0025} = 0.0400 \quad (50)
\end{align}

The lowest working calorific value of combustible gas:
\begin{align}
\dot{Q}(GG)^G_p &= 4.19(2580 \cdot \dot{\mu}(H_2)^G + 3045 \cdot \dot{\mu}(CO)^G + 8517 \cdot \dot{\mu}(CH_4)^G) = 10932.9 \text{kJ/m}^3 \quad (51)
\end{align}

Specific lowest working calorific value of combustible gas:
\begin{align}
\dot{Q}_{spec}^G(GG)_p &= \frac{\dot{Q}(GG)^G_p}{\dot{\rho}(GG)} = \frac{10392.9}{0.816} = 13398.2 \text{kJ/kg} \quad (52)
\end{align}
As follows from calculations, with increasing temperature of pyrolysis, composition and calorific value of the combustible gas does not change since all the water has been used up to the water gas reaction, and no additional reagent is supplied in wood pyrolysis area. But the mole fraction of gases changes. The comparative table shows that with the increase of pyrolysis temperature, hydrogen appears at the output that was not found in the low-temperature pyrolysis.

Table 1. Structure and calorific value of the combustible gas depending on the temperature of wood pyrolysis.

| Parameters                                      | Temperature, °C |
|-------------------------------------------------|-----------------|
|                                                  | 500  | 750  | 1000 |
| Composition of combustible gas in fractions, СО| 0.250 | 0.286 | 0.440 |
| СО2                                             | 0.620 | 0.571 | 0.160 |
| CH4                                             | 0.125 | 0.143 | 0.040 |
| N2                                              | 0.005 | 0.001 | 0.0004 |
| Н2                                              | 0     | 0     | 0.360 |
| The calorific value of combustible gas, kJ / kg| 7650.5 | 8752.1 | 10932.9 |

Table 1 shows that with increasing of pyrolysis temperature from 500 to 1000 °C calorific value of generated combustible gas increases significantly, and is not changed further.

The section from 0 to 300 ° C means removing moisture from wood and beginning of thermal decomposition of wood.

The section from +300 to + 500 ° C means the wood pyrolysis with generation of charcoal, combustible gas with calorific value of about 5000 kJ / kg, vapors of acetic acid, methanol, resins, and other.

The section from + 500 to 750 °C means the formation of charcoal, the thermal decomposition of organic products of pyrolysis to a combustible gas, and an increase in its calorific value to 5431.0 kJ/kg.

The section from +750 to less than 1000 ° C is a transition process on a significant increase in the calorific value of combustible gas to 13398.2 kJ/kg due to the beginning of the water gas flow and expenses of generated charcoal on this reaction.

The section from +1000 to over 1000 °C refers to the process of water gas reaction flow without changing the calorific value of generated combustible gas.

Thus, the developed thermophysical model of pyrolysis of hydrocarbon-containing wastes (on the example of wood) allows speaking about the efficiency of this process and its application for the disposal of hydrocarbon wastes with the expansion of the recycling industry.
3. Conclusion
The TIU developed technologies that reduce the geo-ecological damage to the environment. There was used an integrated systematic approach to the problem of disposal of oil-contaminated hydrocarbon wastes using high-temperature pyrolysis process.

The effectiveness of the technology that we offer is confirmed by comparing the experimental results and theoretical studies. High-temperature pyrolysis technology includes recycling (reuse of gaseous products of pyrolysis), the environmental impact on the atmosphere is reduced (no emissions), water resources and soil cover are not contaminated, landfill areas are decreasing.

The authors identified the effect, that at the thermal processing of hydrocarbon wastes, quantitative correlation between the mass of recyclable wastes, generated pyrolysis gas volume and the time of recycling is observed, proving the great potential of the high-temperature pyrolysis recycling method.

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