Переробка сировини та ресурсозбереження

UDK 665.66:676.0
DOI: 10.33070/etars.3.2021.05

Sezonenko O.B., Vasechko O.O.,
Aleksyeyenko V.V., *Candidate of Technical Sciences,* ***Snihur A.V.***
The Gas Institute of National Academy of Sciences of Ukraine, Kyiv
39, Degtyarivska Str., 03113 Kyiv, Ukraine, e-mail: a-vv@ukr.net, alsez@ukr.net

Investigation of the Processes of Thermal Destruction of Cellulose-containing (Paper) Waste

Materials of practical research work on thermal destruction of paper waste were presented. The main task was The comprehensive study of the aspects of carbon formation on the basis of analytical studies was considered, as well as using a specially built laboratory installation — a waste graphitizer. Research has been carried out on the effectivity of application of pyrolysis gases of the process as fuel to maintain the temperatures of the thermal destruction reaction. Practical examples have proved the possibility and expediency of using the solid residue of the reaction as a component in various fields of production. *Bibl. 10, Fig. 1, Tab. 1.*
Keywords: paper waste, carbon, pyrolysis, gasification, graphitization, utilization.

The formation of municipal solid waste (MSW) in Ukraine as of 2018 only was 49 million cubic meters, or about 11,860,000 tons. Despite the fact that over the past 20 years, the population of Ukraine is constantly decreasing, the formation of household waste is increasing. So the indicator of waste formation in Ukraine on average is 250–300 kilograms per person per year and has a tendency to increase [1, 2].

Quantitative and qualitative characteristics of household waste are not constant and depend on the sources of their formation, seasonality, region, but in general the average percentage of paper and cardboard (cellulose-containing waste) varies from 6 % to 21 % [3, 4]. In addition, if we consider paper or mainly cellulose-containing waste of specialized industries (cardboard and paper mills), their deposit in the total waste balance will be much higher [5].

The standard and widely known solution for utilization of such waste is recycling due to the use of selected and sorted waste paper as secondary raw material [6]. However, in specific cases, such use of paper waste is impossible based on the specifics of their physical properties (short residual fibers, content of toxic substances, high initial moisture, etc.) and economic feasibility (the production process does not allow to lower the grade of the incoming paper). Transportation of such waste groups to solid waste landfills is also not allowed to prevent harmful effects on the environment. For the same reason and based on the requirements of the Ukrainian environmental legislation, which is being harmonized with the European standards in the field of waste management [7], direct combustion of waste is prohibited. Therefore, in such cases, an alternative option is the use of other methods of thermal destruction, such as pyrolysis and gasification. This requires a study of the features of the occurrence of these processes, as well as the possibility and practicality of using the resulting reaction product as a component in various areas of production.

The main component of paper waste is cellulose, chemically a natural polymer −D−glucopyranose and has the chemical formula $[C_6H_{10}O_5]_n$ [8]. The average content of cellulose in the waste is 90 %. In addition, the waste contains up to 2 % melamine-formaldehyde resins (thermosetting oligomeric products of polycondensation of melamine with formaldehyde in the presence of alkaline and acid catalysts). Other in the structure are small impurities, chalk, dyes.

If we consider the utilization of 1,000 tons of paper waste, it contains approximately 900 tons of cellulose and 20 tons of melamine-formaldehyde resins. These compounds can produce heat energy and synthesis gas due to carbon and hydrogen when fully and partially oxidized. The amount of pure carbon when utilized per 1,000 tons of waste will be 400 tons.

The thermal effect of the reaction of the formation of carbon oxide from carbon and oxygen is much less than the thermal effect of the further oxidation of CO to CO_2 [9]. This is explained by the fact that considerable energy must be expended to break the bonds between the carbon atoms in graphite.

The heat effect of the reaction of complete oxidation of carbon to CO_2 from 1,000 tons of waste is 3,148 Gcal [9]. Taking into account efficiency of the thermal unit at the level of 90 %, the actual heat effect will be 2,833 Gcal. Gasification of the same amount of waste will produce 715 tons of carbon monoxide [9], which will give a heat effect of 2,145 Gcal if it is fully oxidized.

Pyrolysis methods, carried out at different temperature levels, pressures and raw material composition, in the presence or without catalysts, are widely used for the utilization of carbon-containing waste. The pyrolysis process (or high-temperature thermolysis) is used to synthesize products of different classes and purposes from hydrocarbons.

Pyrolysis of cellulosic materials has a number of features, which determine the sphere of application of this technology and the products obtained. Thus, during low-temperature pyrolysis of cellulose (up to 350 °C) the glucoside bonds are broken with the initial release of large amounts of gases (CO_2, CO and hydrocarbons) and a liquid distillate, mainly water, containing acetic acid, its homologues and methanol. Then the light and then heavy resins are released. The residue of low-temperature pyrolysis of cellulose is a product similar in composition to charcoal.

During high-temperature pyrolysis of cellulose the output of gas phase increases significantly, and liquid fraction is not observed due to evaporation of liquids and thermal destruction of the original material into simpler components. The content of bound carbon in the residue increases [8, 10].

When the temperature is increased to about 800 °C, due to the pyrolysis of melamine-formaldehyde resin, the waste is transformed into a flammable dispersible powder of black color. With the access of oxygen, the carbon burns out completely, leaving the mineral component.

In order to study the characteristics of the pyrolysis and graphitization process of waste, a laboratory unit was developed and manufactured (Fig. 1).

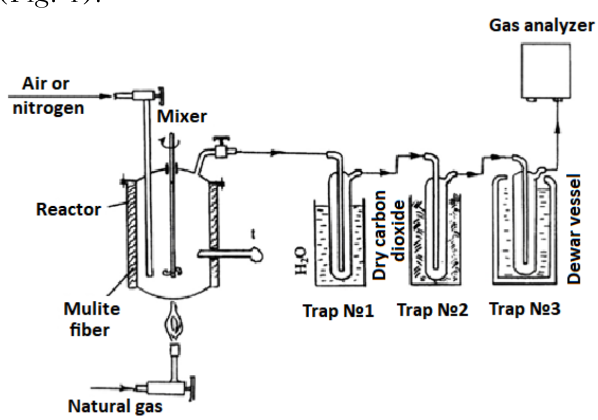

Fig. 1. Scheme of the laboratory unit.

Experiments with pyrolysis at 700 °C of briquetted paper waste were carried out in a 1 liter laboratory reactor made of stainless steel.

Volatile pyrolysis products were captured in traps cooled with water, dry carbon dioxide and liquid nitrogen. The gaseous products that passed the cooled traps were collected periodically in samplers and analyzed by spectrophotometry. The gaseous products were collected in a glass laboratory gas holder.

About 300 g of chopped or briquetted waste was loaded into the reactor. Then, with the air valve closed, the reactor was heated with a gas burner to a temperature of 300 °C, after which the air valve was opened and inert gas (nitrogen) was supplied to the system. Then the temperature was slowly increased to 700 °C and the process was conducted to the stopping of the increase in the level of liquid products in the trap No. 1.

The melamine-formaldehyde resin contained in the paper was mainly pyrolyzed to form water, a heavy resinous liquid, and ammonia (0.1 % by volume). A black flake of loose reaction mass (150 g) was unloaded from the reactor after cooling it to room temperature. Reaction water and a small amount (4.5 g) of liquid combustible pyrolysis products, which have a complex chemical composition, were condensed in trap No. 1. Their analysis was not done.

The gas obtained at the outlet of trap No. 3 was directed to the gas line and used to heat the reactor.

The graphitization process (from 300 °C to 700 °C) is endothermic, so it requires significant energy input.

Based on the above, further experiments were carried out with heating of the reaction mass by heat obtained by burning of pyrolysis products of melamine-formaldehyde resin contained in the waste.

Obtained samples were milled by a bead mill and analyzed by the factory laboratory of the paint and varnish enterprise of Kiev. On the basis of the analysis were determined some of their properties as pigments. Also samples of weather-resistant enamels based on the obtained samples were made and analyzed.

The results of the analyses are shown in Table 1.

Table 1. Properties of the samples of obtained pigments

Name of the enamel indicator	Pattern No. 1	Pattern No. 2	Pattern No. 3	Pattern No. 4
Degree of grinding, мкm	22	35	40	30
Color	black	black	black	olive
Surface	matt	glossy	glossy	glossy
Coating coverage, g/m^2	19,44	25	38	54
Pigment coverage, g/m^2	10	18	23	40
Oil capacity of the pigment, ml/100 g	75,2	140	98,1	63
Gloss, %	5	50	47	50
Drying time, hour	18	18	18	18
Compliance with the normative and technical documentation for PF-115 enamel	+	+	+	+

Comment. Pattern No. 1 obtained by pyrolysis without air access. Pattern No. 2 and pattern No. 3 obtained by graphitization and combustion of half of the carbon. Pattern No. 4 obtained by complete combustion of carbon and further roasting in a muffle furnace at 980 °C.

Conclusions

The importance of recycling cellulose-containing waste is shown. Attention is focused on the impossibility in some cases to use paper waste as secondary raw materials, based on the specifics of individual physical properties of certain wastes. The direction of recycling such wastes by pyrolysis and graphitization process is considered. As an example, the results of a laboratory graphitization unit are presented. It is illustrated that the samples obtained in the graphitization unit correspond to requirements for pigments of weather-resistant enamels. Thus it is shown that the direction of processing of specific types of paper waste not subject to recycling by graphitization is promising because it allows obtaining a quality product for the paint and varnish industry.

References

1. [State Statistics Committee of Ukraine]. — http://www.ukrstat.gov.ua/operativ/operativ2013/ns_rik/ns_u/pzppv_2013_u.html (Ukr.)

2. [National Waste Management Strategy in Ukraine until 2030. Approved by the order of the Cabinet of Ministers of Ukraine dated November 8, 2017 No. 820-р]. — https://zakon.rada.gov.ua/laws/show/820-2017-%D1%80/page#Text (Ukr.)

3. Pohribnyi I.Ya. [Problems of determining the morphological composition of solid waste taking into account modern processing conditions]. *Efektyvna*

ekonomika. [Effective economics], 2012. No. 11. — http://www.economy.nayka.com.ua/ ?op=1&z=1527 (Ukr.)

4. Laznenko D.O. [Determination of parameters of household waste generation in settlements of Ukraine for the purposes of regional planning]. *Swiss-Ukrainian Decentralisation Support Project, Ukraine*. Kyiv, 2019. — https://despro.org.ua/news/detail.php?ID=2166 (Ukr.)

5. [Municipal solid waste in Ukraine: Development potential. Scenarios for the development of solid waste management. Final report]. *Iinternational Finance Corporation in Ukraine,* 2015. — https://www.ifc.org/wps/wcm/connect/region__ext_content/ifc_external_corporate_site/europe+and+central+asia/resources/municipal+solid+waste+in+ukraine+development+potential+scenarios+for+developing+the+municipal+solid+waste+management+sector (Ukr.)

6. Turiab L.V., Kulik L.Y. [Condition and problems of packaging disposal]. *Kvalilohiia knyhy. [Qualification of book].* 2016. No. 2. pp. 94–101. (Ukr.)

7. [Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives]. *[Official Journal of the European Union [UA].* 2008, L312/3-312/30. (Ukr.)

8. Nikitin V.M., Obolenskaya A.V., Shcheglov V.P. [Chemistry of wood and cellulose]. Moscow : Lesnaya promнshlennost', 1978. 368 p. (Rus.)

9. Kazancev E.I. [Industrial ovens. Reference guide for calculations and design]. Moscow : Metallurgiya, 1975. 368 p. (Rus.)

10. Lyamin V.A. [Wood gasification]. Moscow : Lesnaya promнshlennost', 1967. 260 p. (Rus.)

Received June 29, 2021

Сезоненко А.Б., Васечко А.А., Алексеенко В.В., *канд. техн. наук*, ***Снигур А.В.***
Институт газа Национальной академии наук Украины, Киев
ул. Дегтяревская, 39, 03113 Киев, Украина, e-mail: a-vv@ukr.net, alsez@ukr.net

Исследование процессов термической деструкции целлюлозосодержащих (бумажных) отходов

Приведены материалы практической научно-исследовательской работы по термической деструкции бумажных отходов. Рассмотрены энергетические аспекты образования углерода на основе аналитических исследований, а также с применением специально построенной лабораторной установки — графитизатора отходов. Проведены исследования относительно эффективности использования пиролизных газов процесса в качестве топлива для поддержания температур реакции термической деструкции. Практическими примерами доказана возможность и целесообразность использования твердого остатка реакции в качестве компонента в различных сферах производства. *Библ. 10, рис. 1, табл. 1.*

Ключевые слова: бумажные отходы, углерод, пиролиз, газификация, графитизация, утилизация.

Сезоненко О.Б., Васечко О.О.,
Алексєєнко В.В., *канд. техн. наук,* ***Снігур О.В.***
Інститут газу Національної академії наук України, Київ
вул. Дегтярівська, 39, 03113 Київ, Україна, e-mail: a-vv@ukr.net, alsez@ukr.net

Дослідження процесів термічної деструкції целюлозовмісних (паперових) відходів

Наведено матеріали практичної науково-дослідної роботи щодо термічної деструкції паперових відходів. Розглянуто енергетичні аспекти утворення вуглецю на базі аналітичних досліджень, а також із застосуванням спеціально побудованої лабораторної установки — графітізатора відходів. Проведено дослідження щодо ефективності використання піролізних газів процесу як палива для підтримання температур реакції термічної деструкції. Практичними прикладами доведено можливість та доцільність використання твердого залишку реакції як компонента у різних сферах виробництва. *Бібл. 10, рис. 1, табл. 1.*
Ключові слова: бумажні відходи, вуглець, піроліз, газифікація, графітізація, утилізація.

Список літератури

1. Державний комітет статистики України. — http://www.ukrstat.gov.ua/operativ/operativ2013/ns_rik/ns_u/pzppv_2013_u.html

2. Національна стратегія управління відходами в Україні до 2030 року. Схвалено розпорядженням Кабінету Міністрів України від 8 листопада 2017 р. № 820-р. — https://zakon.rada.gov.ua/laws/show/820-2017-%D1%80/page#Text

3. Погрібний І.Я. Проблеми визначення морфологічного складу твердих побутових відходів з урахуванням сучасних умов переробки. *Ефективна економіка*. 2012. № 11. — http://www.economy.nayka.com.ua/?op=1&z=1527

4. Лазненко Д.О. Визначення параметрів утворення побутових відходів у населених пунктах України для цілей регіонального планування. Швейцарсько-український проект «Підтримка децентралізації в Україні». Київ, 2019. — https://despro.org.ua/news/detail.php?ID=2166 (Ukr.)

5. Тверді побутові відходи в Україні : Потенціал розвитку. Сценарії розвитку галузі повод-ження з твердими побутовими відходами. Підсумковий звіт. *International Finance Corporation in Ukraine,* 2015. — https://www.ifc.org/wps/wcm/connect/region__ext_content/ifc_external_corporate_site/europe+and+central+asia/resources/municipal+solid+waste+in+ukraine+development+potential+scenarios+for+developing+the+municipal+solid+waste+management+sector

6. Туряб Л.В., Кулік Л.Й. Стан і проблеми утилізації паковань. *Кваліологія книги*. 2016. № 2. С. 94–101.

7. Директива Європейського парламенту та Ради 2008/98/ЄС від 19 листопада 2008 року про відходи та скасування деяких Директив. *Офіційний вісник Європейського Союзу [UA].* 2008, L312/3-312/30.

8. Никитин В.М., Оболенская А.В., Щеглов В.П. Химия древесины и целлюлозы. М. : Лесная промышленность, 1978. 368 с.

9. Казанцев Е.И. Промышленные печи. Справочное руководство для расчетов и проектирования. М. : Металлургия, 1975. 368 с.

10. Лямин В.А. Газификация древесины. М. : Лесная промышленность, 1967. 260 с.

Надійшла до редакції 29.06.2021