DETERMINATION OF THE FEATURES OF THERMAL DECOMPOSITION OF SUNFLOWER HUSK IN A FLUIDIZED BED

Received Apr. 24, 2024; accepted Jun. 21, 2024
Available online Jul. 01, 2024

Haponych L.¹, Topal O.², Holenko I.³, Kobzar S.⁴

Author for correspondence: Haponych Liudmyla,
e-mail: haponych@ukr.net

Sunflower husk (SH) is a plant waste fuel. The carbon content in different samples of SH ranges from 40.5% to 54.5% in an operating state, with ash content ranging from 1.5% to 8.5%, moisture content ranging from 6.9% to 9.5%, chlorine content ranging from 0.05% to 0.3%, and lower heating value ranging from 14.5 MJ/kg to 20.5 MJ/kg. These characteristics make it a suitable substitute for fossil fuels in power boilers.

Waste-to-energy (WTE) technologies are rapidly developing worldwide, offering the potential for generating renewable energy from waste, including agricultural and food industry waste such as SH. According to our estimates, Ukraine has an annual energy potential of approximately 3.4 million tons of SH or about two million tons of fuel equivalent. Approximately half of this volume is currently being burned in oil extraction plants’ boilers; however, up to one million tons of SH end up in landfills annually, resulting in significant energy losses.

To develop new and improve existing WTE technologies that utilize SH as a fuel source, it’s essential to understand the thermal processing characteristics of SH under conditions similar to those found in different zones within real power boilers - specifically the heating of fuel particles at rates up to 500 °C/s over a temperature range of 500–1000 °C. In this study, we aimed to investigate the thermal processing characteristics by subjecting SH particles within a laboratory fluidized bed reactor to high-speed heating within the aforementioned temperature range.

During rapid heating between 500–1000 °C temperatures range, SH particles undergo conversion into volatile compounds and solid carbon residue. Two distinct stages can be observed on the dynamic yield curves for volatiles. The release and burnout of volatiles occurs during the first stage while the second stage involves coke ash residue burnout. We obtained empirical temperature-dependents for total heat treatment time and carbon residue burnout time under fast heating conditions in the investigated temperature range.

The stage of carbon residue combustion is the most enduring and determines the overall duration of thermal treatment. This stage determines the degree of fuel transformation, especially in cases where low-reactivity carbon residue enters the low-temperature combustion chamber area of the boiler. The obtained regularities have practical significance in designing combustion chambers for thermal processing of sunflower husk.

Keywords: biomass; sunflower husks; waste-to-energy; fluidized bed; heat treatment; pyrolysis; volatiles; carbon residue.
ВІЗНАЧЕННЯ ОСОБЛИВОСТЕЙ ТЕРМІЧНОГО РОЗКЛАДАННЯ ЛУШПИННИ СОНЯШНИКА В КИПЛЯЧОМУ ШАРІ

Гапонич Л.¹, Топал О.², Голенко І.³, Кобзар С.⁴

Автор для кореспонденції: Гапонич Людмила,
e-mail: haponych@ukr.net

Лушпиння соняшника (ЛС) – це паливні відходи рослинного походження. Вміст вуглецю в перерахунку на робочий стан у різних зразках ЛС коливається в межах 40,5–54,5 %, зольності – 1,5–8,5 %, вологості – 6,9–9,5 %, хлору – 0,05–0,3 %, а ниня теплота згоряння в межах 14,5–20,5 МДж/кг. З огляду на вказані характеристики це паливо придатне для використання як замінник викопного палива в енергетичних котлах.

Розробка нових та вдосконалення існуючих технологій перетворення відходів на енергію (WTE), які мають потенціал для отримання відновлюваної енергії з відходів, зокрема сільськогосподарських. За нашими оцінками, щорічний енергетичний потенціал ЛС в Україні сягає 3,4 млн т, або близько 2 млн т умовного палива. Близько половини цього обсягу спалюється в котлах олійноекстракційних заводів, але щорічно до 1 млн т лушпиння потрапляє на звалища, що призводить до значних енергетичних втрат.

Розробка нових та вдосконалення існуючих технологій WTE, що використовують ЛС як паливо, має базуватися на розумінні закономірностей його термічної переробки. Тому метою цієї роботи було дослідження закономірностей термічної переробки ЛС у характерних для різних зон енергетичних котлів умовах – при нагріванні частинок палива зі швидкістю до 500 °С/с в інтервалі температур 500–1000 °С. Така швидкість нагріву була реалізована в лабораторному реакторі киплячого шару.

При швидкісному нагріванні в діапазоні температур 500–1000 °С частинки ЛС перетворюються на газоподібні та твердий залишки. Динамічні криві виходу газоподібних мають два ділянки: перша відповідає виходу і вигорянню газоподібних, а друга – вигорянню вуглецевого залишки. Отримано емпіричні температурні залежності загального часу темдообробки та часу вигоряння вуглецевого залишки Лушпиння соняшника, а також швидкість нагріву палива, що впливає на енергетичні властивості палива.

Радик, відбувається перетворення палива, особливо у випадках, коли низькореакційний вуглецевий залишок потрапляє в низькотемпературну область камери згоряння котла. Отримані результ ativni мають практичне значення при проектуванні камер згоряння котлів термічної переробки лушпиння соняшника.

Ключові слова: біомаса, лушпиння соняшника, перетворення відходів на енергію, киплячий шар, термічна обробка, піроліз, твердий залишок.

The list of used symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR</td>
<td>carbon residue</td>
</tr>
<tr>
<td>CHPs</td>
<td>combined heat and power plants</td>
</tr>
<tr>
<td>FB</td>
<td>fluidized bed</td>
</tr>
<tr>
<td>LHV</td>
<td>lower heating values</td>
</tr>
<tr>
<td>OEP</td>
<td>oil extraction plant</td>
</tr>
<tr>
<td>SH</td>
<td>sunflower husk</td>
</tr>
<tr>
<td>TPPs</td>
<td>thermal power plants</td>
</tr>
<tr>
<td>WTE</td>
<td>Waste-to-energy</td>
</tr>
</tbody>
</table>

¹ канд. техн. наук, https://orcid.org/0000-0003-4611-3193
² канд. техн. наук, https://orcid.org/0000-0002-9458-9420
³ канд. техн. наук, https://orcid.org/0000-0003-3487-8025
⁴ канд. техн. наук, https://orcid.org/0000-0002-8615-4400

12,3 Інститут теплоенергетичних технологій національної академії наук України, м. Київ, Україна
⁴ Інститут технічної теплофізики національної академії наук України, Київ, Україна
Introduction. Sunflower is one of the most widely grown oilseeds in the world. According to the Food and Agriculture Organization of the United Nations, global production amounted to 55 million tons in the 2022/2023 season. In Ukraine, sunflower production reached 15 million tons in the same season [1].

The modern oil and fat complex of Ukraine includes 32 large oil extraction plants (OEPs) and almost a thousand small enterprises and processes about 70% of sunflower seeds. According to the Ukroliyaprom Association, sunflower seed processing reached 13.5 million tons in the 2022/2023 season, resulting in a production of 6 million tons of sunflower oil. The production of sunflower oil generates approximately 15-25% husk waste [2].

Sunflower husk (SH) is a plant-based fuel waste with a carbon content ranging from 40%–55%, and a heating value between 15–21 MJ/kg [3]. Various scientific studies have shown that sunflower husk samples have low ash and sulfur content [4]. Articles [5, 6] have determined that the chlorine content in SH samples ranges from 0.05% to 0.3%. These qualities make SH suitable for replacing organic fuel in both industrial and municipal energy boilers due to their high volatile yield as well as low sulfur and chlorine contents. SH can be burned either uncompressed or compacted into higher-quality biofuels such as pellets or briquettes [7]. Additionally, SH is considered CO₂ neutral fuel.

On April 22nd, 2016, Ukraine signed the Paris Agreement on climate change for 2021–2030 under the United Nations Framework Convention on Climate Change. According to this agreement, majority of countries globally have made commitments to reduce their anthropogenic greenhouse gas emissions with the goal of limiting temperature increases to a maximum of 1.5°C compared to pre-industrial levels. The substitution of fossil fuels with renewable alternatives including biomass, is one of the main focuses in many national decarbonization strategies [8].

The National Action Plan for Renewable Energy Development until 2030 sets an indicative target of boosting the renewable energy share in final energy consumption three times from 9% in 2020 to 27% in 2030, and up to 25% in the electricity sector. In addition, the substitution of organic fuels, such as coal and gas, with eco-friendly fuels becomes more relevant. Waste-to-energy (WTE) technologies have been rapidly developing worldwide and have the potential to recover renewable energy from waste, including agricultural and food industry waste. WTE technologies convert waste matter into various forms of fuel that can be used to supply energy. Waste from agriculture and the food industry, including SH, also has significant renewable energy potential.

According to our estimates, the energy potential of sunflower husks (SH) in Ukraine reaches 3.4 million tons or 2.0 million tons of fuel equivalent. In recent years, approximately 1.7 million tonnes of SH (about half of the annual volume) have been utilized in energy boilers in Ukraine, with 1.3 million tonnes in uncompressed form and 0.4 million tonnes in briquette form [2]. Additionally, 0.2 million pellets are exported each year. However, up to one million tons of sunflower husks end up in landfills annually, resulting in energy losses.

Since 2000, almost all large oil extraction plants (OEPs) in Ukraine have implemented SH combustion technology [9]. Several thermal power plants (TPPs) and combined heat and power plants (CHPs) are currently operational [10]. The largest biomass TPP in Ukraine is the 15 MW Ajax-Dnipro TPP (OEP Potoky, Dnipro), which was commissioned in the summer of 2020. The TPP is equipped with two boilers that produce 35 tons of steam per hour (Kotloenergoiproekt project, Kharkiv) and a Siemens turbine generator. The main fuel used is sunflower husks and husk pellets. The boilers can also run on other types of biomass such as wood chips and waste from sunflower cultivation, transportation, and processing. According to producer data the environmental characteristics of the boilers are as follows: NOx – 100 ppm; CO – 0 ppm; efficiency – 90%; load control range – from 30 to 110%, allowing the TPP to operate in a maneuvering mode.

In 2009, the Kropyvnytskyi OEP’s CHP plant with a capacity of 12.3 MW (33 MW thermal) was equipped with three E-16-3.9-360-D boilers (manufactured in Ukraine) capable of burning sunflower husks with steam capacity of 16 tons per hour. These boilers can also run on natural gas. The electricity and heat generated are used for the technological needs of the OEP.

In 2020, AGL Energy’s oil extraction plant located in Kharkiv region commissioned a biofuel TPP with an electric capacity of 7 MW. This TPP utilizes wood pellets as its primary fuel source. It is equipped with two steam boiler units manufactured by Kharkiv Boiler and Mechanical Plant, each having a steam capacity of 16 tons per year, along with a steam condensing turbine generator manufactured by TRIVENI TURBINE LTD.

In 2012, two solid fuel boilers DKVr-10-23-370 with a steam capacity of 20.0 tons per hour were reconstructed at the CHP plant of Mykolaiv Oil and Gas Processing Plant (Agroindustrial Company EVGROIL) to burn wood pellets. The plant has an electric capacity of 5 MW and a thermal capacity of 10 MW [11]. In 2020, a RAFACO boiler designed to burn sunflower husks was installed at the Zaporizhzhia TPP, which has a capacity of 2.7 MW. ArcelorMittal Kryvyi Rih also uses biofuel burners at furnaces 4-5, where sunflower husks are utilized.

Furthermore, boilers at Ukrainian sugar factories have been converted to burn biomass, including sunflower husks [10]. In 2019, coal boilers manufactured by Babcock-Wilcox in the Kherson region were converted to burn sunflower husk pellets. The Radekhiv Sugar Plant’s BKZ-75GMA boiler uses a grate manufactured by FPM S.A. Mikulov from Poland with a dense layer of direct run. The Haisyn Sugar Plant’s BGM-35M boilers were reconstructed for pellet combustion via the installation of flame-layer furnaces equipped with mechanical feeders.
There are three types of boilers used in the oil and fat industry: 1) modern boilers manufactured by companies such as Vyncke (Belgium), Rafako (Poland), Larget-Badcock (France); 2) new boilers designed and manufactured within Ukraine: 3) old boilers originally designed for fossil fuels but reconstructed for husk combustion even after exceeding their design life [10]. When designing new furnace devices, significant attention is given to the combustion process of the initial fuel particles. The combustion of solid organic fuel particles can be divided into several stages: 1) pyrolysis of the fuel particle, including heating, drying, and release of volatiles; 2) combustion of volatiles and coke residue (CR), including ignition [12]. These stages have different rates, durations, and degrees of influence on combustion depending on the process conditions [13]. The total combustion time for sunflower husks (SH) can be represented as a sum of two time intervals corresponding to: 1) release and combustion of volatiles, and 2) combustion of CR [14, 15].

Pyrolysis of biomass is the direct thermal decomposition of organic components with the production of CR and volatile liquids (tars) and gaseous products [16]. This complex process involves multistage reactions, complex chemical pathways, highly unstable intermediate products as well as heat and mass transfer effects. The volatile fraction includes combustible components such as H₂, CH₄, CO₂ along with small amounts of C₂H₆, C₅H₁₀ higher hydrocarbons, and water vapor [13]. The volatiles formed during thermal decomposition significantly influence subsequent ignition processes. Higher yields of volatiles in initial fuels result in faster ignition rates for CR leading to more intense burning. Heating rates during pyrolysis also affect the ratio between volatiles' yield (both gaseous and liquid) to coke residues. Depending on heating rates slow or fast pyrolysis can be distinguished.

The yield and combustion of volatiles, which precede the combustion of CR, can hinder the diffusion of the oxidizer to its surface [17]. This is because the intense saturation of the boundary layer adjacent to the particle with volatiles leads to the formation of a gas mixture of fuel and oxidizer in it. The combustion of this mixture leads to a sharp decrease in the concentration of oxidizer on the surface of the coke particle. As a result, the coke residue hardly participates in the ignition and combustion process at the initial stage, leading to a phenomenon known as homogeneous-heterogeneous ignition.

Biomass is a very complex fuel consisting of many components. The three main organic components of biomass are cellulose, hemicellulose, and lignin [18]. Cellulose is a carbohydrate polymer composed of glucose monomers – polysaccharides with a chemical formula C₆H₁₀O₅ [19]. Its structure includes five carbon atoms forming a ring structure with attached H and OH groups, while oxygen occupies another angle [20]. Due to its high degree of hydrogen bonding, cellulose is resistant to chemical degradation [21]. It serves as the main structural component in most terrestrial biomass [22]. Within the lignocellulosic complex, cellulose retains its crystalline fibrous structure and acts as its core. Many properties exhibited by cellulose depend on its polymerization degree i.e., the number of glucose molecules that make up one polymer molecule.

Hemicelluloses is a collective term used to describe a wide range of heteropolysaccharides, such as xylan. The chemical formula of a hemicellulose molecule is (C₆H₁₀O₅)n [12]. Hemicellulose is an amorphous organic polymer that decomposes more rapidly than cellulose when exposed to heat, and its thermal decomposition begins at lower temperatures [22]. Hemicellulose is a mixture of various polymerized monosaccharides and can be relatively easily hydrolyzed into its constituent sugars.

Lignin, on the other hand, is a large hydrophobic (mostly aromatic) polymer composed of phenolic monomeric units linked together in a three-dimensional structure [23]. Its chemical formula is [C₆H₅O₆S(OCH₃)]₀.₃–₁.₇₇₃ [24]. Lignin is the second most abundant organic material on Earth after cellulose. It provides the framework, in which cellulose and hemicellulose are embedded [25]. While most lignin is found in the middle lamella where it serves as support for plant cell walls, there may also be smaller amounts located on the cell surface.

As a general rule, cellulose is the most abundant natural polymer, accounting for 35%–55% of biomass [26]. Hemicellulose is the second most abundant natural polymer, accounting for 20%–40% of mass, followed by lignin, which makes up 10%–30% of lignocellulosic biomass. The content of each component varies for different types of biomasses, as well as between different parts of the same type of biomass. For example, sunflower seeds, husks and stalks are characterized by different compositions of cellulose, hemicellulose and lignin. As a result, they have different elemental compositions and lower heating values (LHV).

The structural composition of sunflower husks also varies between different cultivars [27]. SH generally contain approximately 30%–48% wt. cellulose, 34%–38% wt. hemicellulose, and 17%–26% wt. lignin [28]. The elemental composition of the fuel and the amount of volatiles (which affects LHV) can also vary depending on the structure.

Chemical analysis has shown that SH contains approximately 14%-18% bound carbon, 70%-76% volatiles, and 6%-10% moisture [29]. Table shows the elemental composition of the operating state and LHV from various samples of SH: 1 - [4], 2 - [3], 3 - [6], 4 - [10], and 5 - [30]. Different samples of SH have a content (on the operating state of fuel) of carbon C’ = 40.5%-54.5%, sulphur S’ = 0.1%-0.2%, chlorine Cl’ = 0.05%-0.3%, ash A’ =1.5%-8.5%, and moisture W’ =7.0%-9.5%. The lower heating values range from 14.5 to 20.5 MJ/kg. The high lignin content in biomass is associated with LHV since lignin contains approximately 30% higher heating value than cellulose and hemicellulose [29]. Sunflower husks have a high LHV due to their high lignin content.
The pyrolysis rate of biomass is considered to be the sum of the rates of the main components: cellulose, hemicelulose, and lignin [21]. Each component contributes to this rate in proportion to its contribution to the composition of the biomass [31]. Interactions between biomass components have a negligible effect on pyrolysis results.

The mechanism of the chemical reaction of lignocellulose pyrolysis is not fully understood and remains ambiguous and controversial. Pyrolysis of lignocellulose is a complex process involving multiphase reactions, intricate chemical pathways, highly unstable intermediate products, and the effects of heat and mass transfer. The pyrolysis of hemicellulose and cellulose occurs in three stages. The first stage is an intramolecular dehydration process that leads to the formation of anhydrocelluloses. This process is weakly endothermic and occurs at a temperature around 220°C. The second stage involves the production of levoglucosan, which is an endothermic process occurring at a temperature around 280°C. The third stage involves numerous reactions leading to the cleavage of C–C and C–O bonds as well as radical reactions that form gases or volatile compounds, mainly through the decomposition of anhydrocelluloses. The breaking of glycosidic bonds in cellulose R–O–R, R-radical occurs at temperatures between 300°C and 500°C [22].

Since lignin is an aromatic polymer, kinetic models that are valid for cellulose cannot be applied to it. Lignin is usually considered the most stable of the biomass components. However, lignin undergoes weak decomposition at very low temperatures and is less stable than cellulose at the initial stages of decomposition. This initial instability of lignin is likely related to the breakage of side groups that form the lignin polymer. Due to the structural similarity between lignin and coal, some models developed for coal pyrolysis can be applied to lignin pyrolysis. Obviously, direct extrapolation of results obtained with coal, cellulose, and lignin to the pyrolysis of specific biomass is possible only for qualitative analysis and evaluative calculations.

Primary pyrolysis of biomass begins with dehydration at temperatures below 200 °C, while secondary pyrolysis (destruction and synthesis), which includes the aromatization process, begins at temperatures above 400 °C [32]. The initial decomposition temperatures of biomass range from 220–240 °C with significant structural modifications occurring between 350 °C and 400 °C [13]. These modifications are characterized by a reduction in intensity in C–O and C=C bonds formation as well as alkyl bond C–C formation increases. As the temperature increases, there is a continuous decrease in the intensity of the valence bonds -OH and an increase in the production of aromatic compounds. The maximum yield of these compounds is observed at temperatures above 600 °C and depends on the ratio of cellulose to lignin in the fuel.

The temperature dependence of mass loss during pyrolysis of different biomass samples is characterized by two stages. The first stage involves the decomposition of hemicellulose at temperatures between 250–300 °C and cellulose at temperatures close to 350 °C [33]. The second stage is associated with lignin decomposition, which occurs at higher temperatures [34]. While the characteristic pyrolysis temperatures are similar for different types of biomasses, the amount of volatile yield at each stage depends on the type of biomass, specifically on its ratio of cellulose, hemicellulose, and lignin, as well as the elemental composition of the biomass.

The regularities of fast high-temperature pyrolysis of biomass and the simultaneous combustion of its coke residue have not been sufficiently studied. Most biomass pyrolysis studies focus on the results of thermogravimetric analysis [23]. Thermogravimetric analysis is a method that records the weight loss of a sample against temperature under controlled heating rate and gas atmosphere. Differential thermogravimetric analysis curves are derived from thermogravimetric curves and are widely used to evaluate pyrolysis kinetics in biomass [13]. These methods provide data in the form of kinetic information at a low heating rate (2–30 °C/min.). In the articles [31, 33], the fast pyrolysis of biomass in a fluidized bed was studied, but the dynamic characteristics of the process were not determined. The article [35] investigated the fast pyrolysis of isolated components of biomass. It was found that the maximum volatile hemicellulose yield occurs at layer temperatures above 500 °C, while lignin yield is maximized above 800 °C. H₂O, CO₂, and CO make up the largest fractions of all three

The elemental composition and lower heating values of different samples of sunflower husks

<table>
<thead>
<tr>
<th>Sunflower husks samples</th>
<th>The elemental composition of the operating state, %</th>
<th>LHV, MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W', %</td>
<td>A', %</td>
</tr>
<tr>
<td>1</td>
<td>6.9</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>7.7</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>9.3</td>
<td>8.5</td>
</tr>
<tr>
<td>4</td>
<td>9.5</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>9.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*sum of organic and sulphide sulphur or pyritic; **according to our calculations
biomass components at all the temperatures studied. In the study [36], it was found that for fast pyrolysis, the maximum volatile yield for hemicellulose occurs at a temperature of 550 °C, for cellulose at 700 °C, and for lignin at 900 °C and above.

The transfer of the results of existing studies on the pyrolysis of individual components of lignocellulose to real biomass will inevitably result in some inaccuracies. However, the established patterns allow us to interpret the results of experimental studies on the thermal degradation of real biomass. We have not found any studies on the fast pyrolysis of sunflower husks.

**Setting of tasks.** According to the Recovery and Development Plan of Ukraine (part of the United 24 initiative), renewable energy development plays a crucial role in shaping the future structure of Ukraine’s power system. The Energy Strategy of Ukraine aims to increase the use of renewable fuels, including agricultural and food industry waste. To achieve this, it is necessary to improve existing waste-to-energy (WTE) technologies and develop new ones for the incineration of agricultural and food industry waste [37]. These efforts should be based on the thermal processing characteristics of such fuels [38]. It is worth emphasizing that the waste from oil extraction plants, such as sunflower husks, holds particular interest due to its suitability as a substitute for fossil fuels in power boilers. As mentioned earlier, its annual energy potential in Ukraine amounts to 3.4 million tons.

The aim was to determine the dynamic regularities of thermal decomposition for SH particles across a wide temperature range. The study focuses on investigating the thermal processing patterns of SH under conditions representative of different zones in energy boilers. In boiler units, fuel particles undergo high heating rates and process temperatures. Therefore, it examines heating fuel particles at rates up to 500 °C/s within a temperature range of 500-1000 °C. To achieve these heating rates, experimental research was conducted using a fluidized bed (FB) system.

**The characteristics of the investigated fuel.** Waste from the production of the Pology Oil Extraction Plant in the Zaporizhzhia region of Ukraine was chosen for the study. The initial samples used in the study were intact halves of solid sunflower seed shells with sizes ranging from 10-14 mm. The average technical analysis results for sunflower husks are as follows: ash content in dry state (A_d) is 2.4%, volatile yield to dry ash-free state (Vdaf) is 76.8%, moisture per operating state (W_p) is 10.2%. The lower heating value is measured at 20 MJ/kg. The husk material was not subjected to any pre-treatment or particle size modification during experiments.

The following standard methods were used to determine the lower heating value and technical parameters of sunflower husk samples: ISO/CD 21645: Solid recovered fuels — Determination of ash content; CEN/TS 15414-1:2010: Solid recovered fuels — Determination of moisture content using the oven dry method — Part 1: Determination of total moisture by a reference method.

**Fluidized bed reactor.** FB reactors are commonly used for thermal processing of various materials, including sunflower husk. In this study, the dynamics of SH thermal processing were investigated using a laboratory setup consisting of a vertically positioned quartz reactor with a pseudo-fluidized bed. The reactor had an internal diameter of 0.05 m and a height of 0.9 m. To achieve optimal heating conditions, it is important to control the rate at which temperature changes occur in the reactor. Heating rates between 250 and 500 °C/s were implemented in this study.

Before conducting combustion experiments, preliminary tests were conducted on a "cold" model to determine the air flow rate required to create pseudo-fluidization conditions for the husk particles. Pseudo-fluidization refers to when particles behave like fluid in response to an upward-flowing gas stream. The results showed that increasing the air flow rate did not result in pseudo-fluidization of the husk particles until a certain threshold value was reached. Instead, the particles formed a weak-moving layer that acted as a filter. However, once this critical flow rate (linear velocity) was exceeded, intensive removal of particles from the reactor occurred. Based on these observations, it was concluded that sunflower husk particles belong to group A materials [39], which are unable to undergo pseudo-fluidization without the presence of layer-forming material. Therefore, pre-burned sand with particle sizes ranging from 0.05-0.63 mm and heated to 950 °C was used as an inert material for subsequent combustion experiments involving SH particles.

The addition of pre-burned sand facilitated intense mixing between SH and sand particles within the reaction zone while ensuring uniform access of oxygen to fuel particles during combustion’s final stage. This approach helped avoid concentration gradients along the husk layer (when airflow rates were below entrainment velocity) and potential uncertainties caused by uncontrolled entrainment from reaction zones (near swirling speed boundaries).

In summary, studying combustion dynamics in FB reactors requires careful consideration of particle characteristics such as their ability for pseudo-fluidization and implementing appropriate measures like using layer-forming inert materials for achieving uniform mixing and controlled reactions.

**Experimental procedure.** During the experiments, the air flow rate was chosen based on the pseudo-fluidization condition of sand particles with a size range of 0.05-0.63 mm. Initially, 50 grams of inert material (sand) were loaded into the reactor to create a boiling layer at an air flow rate (G_ airflow) ranging from (91–104)-10^6 m^3/s, corresponding to air...
velocities \((w_{\text{air}})\) of 0.15-0.18 m/s. The reactor was vertically installed in an electric tube furnace with a power output of 2.5 kW. The temperature of the layer was measured using a type K thermocouple (Chromel-Alumel), which was placed within the layer for accurate temperature monitoring.

After heating and stabilizing the layer temperature, a known weight of sunflower husk was introduced into the reactor through a gate system. Under these conditions, rapid heating and subsequent reaction of the husk took place at the predetermined layer temperature. The combustion experiments were conducted at atmospheric pressure within a range of layer temperatures from 500 to 1000 °C with intervals of 100 °C. The volatile products resulting from thermal destruction of the husk were carried upwards by airflow and passed through several stages including a bubbler, condensate collector (to delay condensation), fine filtration packing, and finally entered into a mass spectrometer connected to specialized analog-to-digital converter equipment controlled by a personal computer for data acquisition and processing using specific techniques. This way, valuable information about combustion characteristics such as gas composition and evolution rates during sunflower husk combustion could be obtained.

Gas analysis methodology. The gas analysis methodology described here utilizes a mass spectrometer with six channels to measure the concentration of specific gases in a gas mixture at a pressure of 0.1 MPa. The output voltage of each channel is linearly related to the concentration of the corresponding gas. The measurement system is able to continuously determine and store partial pressures \((p_i)\) of CH\(_4\), CO, CO\(_2\), H\(_2\), O\(_2\), and Ar. During the measurements, data is continuously monitored and recorded in dynamic curves that represent the component composition (partial pressure) of these gases over time \([\text{CO, CO}_2, \text{CH}_4, \text{H}_2, \text{O}_2, \text{Ar}] = n(t)\). The collected data can then be further analyzed to determine the characteristic time for the pyrolysis and combustion of volatiles, as well as the time required for the combustion of residual coke. This methodology provides valuable insights into the behavior and pyrolysis/combustion properties of different gases in a gas mixture.

Measurement instrument errors. The main parameters directly measured in the experiments were temperature, pressure, gas flow rates, and volumetric fractions of gaseous components. For each of these parameters, the types of measuring instruments and the allowable relative measurement errors \(\delta_i\) (according to the instrument specifications) are provided below.

Temperature: Thermocouple transducers type TXA(K), measurement range 200-1300 °C, with a constant \(\delta_i = 0.75\%\) within the range of 500-1000 °C. Pressure: Sample spring gauge type MO, measurement range for excess pressure 0-2.5 MPa, with a constant \(\delta_p = 0.5\%\). Gas flow rates: Rotameters types RM A-0.1 GUZ (for tracer gas), RM-0.63 GUZ and RC-3 (for carrier gas), with a normalized \(\delta_i = 2.5\%\), based on scale length. Volumetric fractions of gaseous components: Magnetostatic mass spectrometer type MX-1215, measurement ranges 0-20\% (Ar and CH\(_4\)) and 0-100\% (other components), with a \(\delta_i = 2.5\%\) for the upper value.

It is worth noting that for computer registration of temperatures and volumetric fractions of gaseous components, a multi-channel ADC with a step size of 1/1024 was used per channel’s range. Taking into account the ADC’s step size, it can be considered that additional errors were practically not introduced during direct measurement registration.

Dynamic errors. During the experiment, the pressure in the reactor and the flow rate of the tracer gas remain constant, while the temperatures vary by no more than 2 °C between the two measurements. This allows us to consider the dynamic error of measuring these parameters negligible. As for the volumetric fractions of gas components \(\Pi_i\), it is taken into account that according to the technical description of mass spectrometer MX-1215, its measurement time constant is up to 0.5 s (including integration of gas composition in the inlet system). Therefore, \(\Pi_i\) values are measured with a step size of 0.005 s for each mass spectrometer channel and averaged values are recorded every 0.5 s. The recorded dynamic curve of output impulses represents a histogram. The dynamic characteristics of the process were considered reliably measured at timescales exceeding 5 s.

Other errors. Among the factors that contribute to additional difficult-to-account-for measurement errors, the following should be mentioned: variations in the ash content and moisture content in low-mass samples, uneven gas carrier flow rate during manual adjustment of the output flow valve, temperature gradient throughout the reaction zone volume, possible uneven accessibility of gas carrier flow to LS particles, etc. The errors caused by these factors are considered random [40], and the results are statistically processed using the EXCEL software package with an approximation selected in each case to maximize correlation with experimental data points.

Results and discussion. During pyrolysis, a portion of the husk mass is converted into volatile matter, while the remaining portion (up to 20%-30% of the initial mass) forms a solid coke residue, which is characterized by low reactivity and high strength. Fig. 1 presents the dynamic curves of partial pressures of gas products generated during the combustion of a discrete sample of sunflower seed husks weighing of \(m = 0.1\) g at a temperature of \(T = 500\) °C. In comparative experiments, the mass of the sunflower husk sample was kept constant for all temperatures studied. The figure shows that the dynamic curves for CO\(_2\) and CO have
two fundamentally different sections. The first section corresponds to the release and combustion of volatiles, while the second section corresponds to the combustion of the carbon residue. The first section has a pronounced maximum. The duration of the initial section (up to the maximum) depends on the duration of the sequentially-parallel stages of fuel particle heating and mixing in the fluidized bed. In the specified experiments, the initial section before the maximum is 2–3 seconds, and its duration slightly decreases with an increase in the bed temperature.

The second stage, which is the burning of carbon residue, is longer compared to the release and burning of volatiles. The point where the CO\textsubscript{2} curve changes direction can be chosen as a convention to distinguish between the end of the pyrolysis stage and the beginning of the carbon residue burning stage. It can be observed that the process of burning carbon residue is accompanied by a slow release of CO\textsubscript{2} until it reaches a quasi-steady state level. This trend was observed for all investigated temperatures and indicates a reduced reaction rate of carbon coke from sunflower husks with oxygen in the air, especially at the final stages of combustion (conversion). The release and combustion of volatiles counteract the diffusion of oxidizer to the surface of fuel particles. This is explained by the intensive saturation of boundary film adjacent to carbon residue particles with volatiles, leading to the formation of vapor-gas mixture consisting of combustible components and oxidizer. When it burns out, the concentration of oxidizer on the surface of the carbon residue sharply decreases, and as a result, the residue is almost not involved in ignition and combustion processes at the initial stage. Homogeneous-heterogeneous ignition is realized. The observed fact may indicate the presence of significant mechanical unburned residue of sunflower husk material due to a mismatch between the time it spends in the combustion chamber and the time necessary for the complete combustion of coke residue to the required degree of conversion.

For layer temperatures up to 900 °C, the aforementioned trends persist: the dynamic curves (for CO\textsubscript{2} and CO) have two distinct segments, one of which corresponds to the release and combustion of volatiles, while the other corresponds to the combustion of carbon residue (Fig. 2). Throughout the entire range of investigated temperatures, the longest stage of combustion for sunflower husk particles is the combustion of carbon residue: 22–23 seconds at 500 °C; 14–15 seconds at 600 °C; 11–12 seconds at 700 °C; 10–11 seconds at 800 °C; 9–10 seconds at 900 °C; and 6–7 seconds at 1000°C. Increasing the layer temperature also leads to a decrease in the total burning time of sunflower husk particles, mainly due to a reduction in the burning time of carbon residue. Therefore, this stage in combustion chambers is recommended to be conducted at temperatures above 800-900 °C.

An increase in temperature in the reaction zone is accompanied by an increase in the recorded peaks of methane and hydrogen at the pyrolysis stage: at T = 500 °C for H\textsubscript{2} up to 0.8% vol. and for CH\textsubscript{4} – up to 0.14% vol.; at T = 700 °C for H\textsubscript{2} up to 1.2% vol. and for CH\textsubscript{4} up to 1.0% vol.; at T = 800 °C for H\textsubscript{2} and CH\textsubscript{4} up to 2.0% vol.; at T = 900 °C for H\textsubscript{2} and CH\textsubscript{4} up to 2.5% vol. The observed increase in the yield of CH\textsubscript{4} and H\textsubscript{2} with increasing temperature during sunflower husk pyrolysis qualitatively matches the results of previous studies on fast pyrolysis of olive kernels, as well as isolated biomass components such as hemicellulose, cellulose, and lignin [33, 35].
Fig. 2. The dynamics of the release of gaseous components during the combustion of SH samples at a temperature of $T = 900^\circ C$ and an air flow rate of $G_{\text{air}} = 103.7 \text{ ml/s}$ ($w_{\text{air}} = 0.18 \text{ m/s}$)

It should be noted that distinguishing between volatile burning stages and carbon residue burnout becomes difficult when temperatures exceed $900^\circ C$ based on dynamic curve analysis (Fig. 3).

In addition to a comprehensive study on the pyrolysis-combustion process conducted in these experiments, it is necessary to separately investigate pyrolysis in an inert environment as well as carbon residue burnout in an oxidizer. One disadvantage of this analysis is that coke preparation conditions may influence its subsequent burnout; however, a clear advantage is the ability to divide the process into distinct stages.

Fig. 3. Dynamics of volatile gases emission during thermal processing of SH samples at a temperature of $1000^\circ C$

The study enabled the determination of the main patterns of pyrolysis and burnout of SH during rapid heating to a temperature of $1000^\circ C$. A notable characteristic of SH, which influences its thermal decomposition, is its lignocellulosic structure. During pyrolysis in a fluidized bed, the maximum yield of volatile hemicellulose occurs at approximately $500^\circ C$, cellulose at $700^\circ C$, and lignin at $900^\circ C$.

The highest proportions of $\text{H}_2$, $\text{CO}_2$, and $\text{CO}$ are observed for all three biomass components across all studied temperatures. This can be attributed to the fact that hemicellulose and
Cellulose contains around 45%-50% wt. oxygen while lignin contains about 25%-30% wt. Consequently, hydrocarbons produced during pyrolysis rapidly react with oxygen radicals generated within the process and undergo oxidation.

The initial stage of thermal processing of SH involves the degradation of hemicellulose. At temperatures ranging from 220-280 °C, intramolecular dehydration occurs, resulting in the formation of anhydrocellulose [22]. During this process, weakly bound impurity groups, primarily consisting of CO, CO₂, and H₂O, are released. Significant structural modifications occur between 350-400 °C as evidenced by a decrease in intensity and the breaking of C-O and C=C bonds [13]. Additionally, alkyl bonds (C-C) are formed during this stage. The production of CH₄ begins at 400 °C and increases as the temperature rises [36]. The proportions of CO, H₂, and CH₄ in the total volatile yield increase with temperature while H₂O gradually decreases [35]. Fig. 4 illustrates an increase in the partial pressure of H₂ with rising temperature.

\[ \text{Fig. 4. Partial pressures of H}_2 \text{ for the temperature range 500–1000 °C} \]

Within the temperature range of up to 500 °C, bonds between monomolecules are broken, and the material loses plasticity and becomes brittle [22]. With an increase in temperature, the intensity of valence bonds –OH decreases continuously, and there is an increase in the yield of aromatic compounds. The maximum yield of these aromatic compounds depends on the ratio of cellulose to lignin in the fuel and is typically observed at temperatures above 600 °C [35].

In the temperature range of 450–600 °C, the ring structure of lignocellulose molecules breaks along oxygen heteroatoms (O) and forms linear (aliphatic) radicals [36]. This leads to numerous reactions involving the splitting of C-C and C-O bonds as well as radical reactions that result in the formation of gases or volatile compounds. These reactions primarily occur due to the decomposition of anhydrocellulose [22]. Light peripheral groups such as СН₂, H, OH break off from these molecules and are released in gaseous form.

With rapid heating, detachment of light functional groups and degradation occur simultaneously. The yield of gaseous products depends on the environment. In an oxidizing atmosphere (as in the conducted experiments), light H- and CO₂ groups quickly combine or undergo oxidation, resulting in an increased proportion of CO₂ in the pyrolysis products.

As the pyrolysis temperature further increases, more bonds break down into the initial substance, leading to an increase in small radical fragments and ultimately increasing the yield of gas phase products.

Based on experimental data, both total heat treatment time (Fig. 5) and time required for complete combustion of carbon residue from sunflower husk were determined for temperatures ranging from 500 to 1000 °C.

The results for the temperature range of 500-1000 °C were summarized in the form of empirical equations. For the total heat treatment time (τ), the equation is

\[ τ = 415.0 \times T^{1.55} \pm 2.0 \]

where T is the layer temperature in °C. The equation for the time required for complete combustion of carbon residue from sunflower husk is

\[ τ = 572.0 \times T^{1.64} \pm 1.5 \]

where τ represents the burnout time of husk particles in seconds.

The proposed equations have an average error of less than 1.8%.

In the temperature range of 600-1000 °C, an empirical equation for the total heat treatment time can be used:

\[ τ = 160.0 \times T^{1.4} \pm 2.2 \]

with an average error of 2%.
For temperatures ranging from 700-1000 °C, there is a linear relationship between the total heat treatment time and process temperature: \( \tau = 28.0 - 0.019 \times T \pm 1.7 \), with an average error of 1.5%.

![Graph showing temperature dependence of total heat treatment time of sunflower husk samples on temperature](image)

**Fig. 5. Temperature dependence of the total heat treatment time of sunflower husk samples on temperature**

**Conclusions**

1. Sunflower husks are plant-derived fuel waste. The carbon content in different samples of lignocellulosic biomass ranges from 40%-55% by dry weight, with a heat of combustion ranging from 15-21 MJ/kg. The characteristics of high volatile yield, low sulfur content, chlorine, ash, and moisture make it suitable for replacing fossil fuels in industrial and municipal energy boilers. According to our estimates, the annual energy potential of SH in Ukraine is 3.4 million tonnes or 2.0 million tonnes of equivalent fuel.

2. Thermal treatment of sunflower husks is a complex of physicochemical processes that can be conditionally divided into the following sequential-parallel stages: 1) pyrolysis, which includes heating, drying, formation and release of volatiles; 2) combustion of volatiles and solid carbon residue. The volatile substances include \( \text{H}_2, \text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2\text{O} \) and a small amount of \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \). These stages have different speeds, durations and degrees of influence on combustion depending on the technological conditions of the process and the type of fuel.

3. Sunflower husk is a complex multicomponent fuel containing approximately 30%-48% cellulose, 34%-38% hemicellulose, and 17-26% lignin by mass. Depending on the structure, the elemental composition of the fuel varies as well as the quantitative and qualitative composition of volatiles and, as a result, the heat of combustion. In addition, different molecular structures of individual components lead to different decomposition mechanisms during pyrolysis. The major components of volatile sunflower husks at temperatures ranging from 500-1000 °C are \( \text{H}_2\text{O}, \text{CO}_2 \), and CO. This can be explained by the fact that cellulose and hemicellulose contain approximately 45%-50% oxygen by mass, while lignin contains about 25%-30% oxygen by mass. The yield of gaseous products depends on the environment. In an oxidizing environment (as in the conducted experiments), the light H and CO groups quickly combine or oxidize, resulting in an increase in the proportion of \( \text{CO}_2 \) in the gaseous reaction products. As the temperature increases, the number of bond breaks in the feedstock and small radical fragments increases, leading to an increase in gas phase yield.

4. Dynamic curves describing volatile yields exhibit two distinct stages: the first region corresponds to the release and combustion of volatiles, while the second region corresponds to the combustion of carbonaceous residue. Upon its combustion, there is a sharp decrease in oxidizer concentration on the surface of carbonaceous residue, which consequently has little involvement in ignition and burning processes during the initial stage. Homogeneous-heterogeneous ignition is realized. The combustion of CR is considered as the dominant process in thermal decomposition of SH particles, which is also characterized by longer duration and determines overall burning time. Increasing the layer temperature leads to a decrease in the total burning time of SH particles, mainly due to a reduction in the burning time of CR.

5. The stage of carbon residue combustion is the longest and determines the overall duration of thermal treatment. This stage determines the degree of fuel conversion, especially in cases where low-reactivity carbon residue enters the low-temperature zone of the boiler combustion chamber. Empirical temperature dependencies were obtained.
for the overall duration of thermal treatment and the duration of CR combustion during rapid heating in the temperature range of 500-1000 °C. These regularities are practically significant in designing combustion chambers for thermal processing boilers for SH.

REFERENCES


