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RESEARCH OF COMMON OAK ACORNS USE FOR ALTERNATE SOLID FUEL PRODUCTION

Oleksandr S. Ivashchuk*, Volodymyr M. Atamanyuk, Roman A. Chyzhovych,
 Vladyslava A. Manastyrska, Serhii A. Barabakh, Iryna B. Sobechko
 Lviv Polytechnic National University, 12 Bandery str., Lviv, 79013, Ukraine
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Abstract

The article presents the experimental studies results of solid fuel production from fruits of common oak (*Quercus robur*). The calorific value, ash content, and moisture content of the initial plant material and the briquetted solid fuel samples were studied. The value of the highest calorific value for unformed raw materials is ~18163 kJ/kg, and for briquettes ~17428 kJ/kg. The data obtained indicate the prospects of using the common oak (*Quercus robur*) acorns as a raw material for the production of alternative solid fuels. The value of ash content for unformed raw material is ~0.93 % wt., and for briquettes ~1.22 % wt. The moisture content of all obtained briquetted samples was <1% wt. The data obtained indicate the prospects of using acorns of *Quercus robur* as a raw material to produce alternative solid fuels, since the parameters are close to existing European standards. The use of alternative solid fuel from acorns can improve the environmental situation by replacing traditional fuel resources and may be one of the ways to rationally use renewable natural raw materials.

Keywords: biomass; alternate solid fuel; briquettes; acorns; common oak; *Quercus robur*.

ДОСЛІДЖЕННЯ ВИКОРИСТАННЯ ЖОЛУДІВ ДУБУ ЗВИЧАЙНОГО ДЛЯ ВИГОТОВЛЕННЯ АЛЬТЕРНАТИВНОГО ТВЕРДОГО ПАЛИВА

Олександр С. Івашук, Володимир М. Атаманюк, Роман А. Чижович,
 Владислава А. Манастирська, Сергій А. Барабах, Ірина Б. Собечко
 Національний університет "Львівська політехніка", вул. Бандери 12, Львів, 79013, Україна

Анотація

У статті подано результати дослідження одержання альтернативного твердого палива із плодів дубу звичайного (*Quercus robur*). Досліджено теплотворні характеристики, зольність та залишкову вологість вихідної рослинної сировини та створених брикетованих зразків твердого палива. Значення вищої теплотворної здатності для несформованої сировини становить ~18163 кДж/кг, а для сформованих брикетів ~17428 кДж/кг. Отримані дані свідчать про перспективність використання жолудів дубу звичайного (*Quercus robur*) як сировини для виготовлення альтернативного твердого палива. Значення зольності для несформованої сировини становить ~0.93 % мас., а для сформованих брикетів ~1.22 % мас. Вміст води в усіх отриманих брикетованих зразках становив <1% мас. Отримані дані свідчать про перспективність використання жолудів *Quercus robur* як сировини для виготовлення альтернативного твердого палива, оскільки показники близькі до існуючих європейських стандартів. Використання альтернативного твердого палива із жолудів може дозволити покращити екологічну ситуацію шляхом заміни традиційних паливних ресурсів та може бути одним із способів раціонального використання відновлюваної природної сировини.

Ключові слова: біомаса; альтернативне тверде паливо; брикети; жолуді; дуб звичайний; *Quercus robur*.

*Corresponding author: +380322582657 e-mail: oleksandr.s.ivashchuk@lpnu.ua

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Introduction

The current deterioration of the ecological situation and the state of the environment requires a search for a rational replacement for traditional natural resources. Among the forefronts of this exploration is the repurposing of plant materials, offering promising avenues for sustainability. Harnessing previously overlooked renewable resources often requires minimal additional investment or intervention, leveraging the unique geographical characteristics of local ecosystems.

For example, the common oak (or the pedunculate oak, the European oak; the binomial name – *Quercus robur*) plays a pivotal role in the formation of the forest cover of deciduous forests in Ukraine. Oak plantations cover 46% (approximately, 284000 hectares) of the total forest area in the northeastern region [1]. According to [2; 3], in 2020, the total number of acorns was 9900÷19000 per hectare with a total weight of 26.8÷54.1 kilograms per hectare, and in 2021–8600÷17200 per hectare with a total weight of 22.7÷48.4 kilograms per hectare – highlighting the untapped potential for sustainable resource utilization.

At the same time, the fruits of this tree, acorns, have significant potential for use in various areas of economic activity, given that they can be considered as low-cost renewable plant material. They are classically used as animal feed, in particular, for pigs [4]. It is also known that acorns have significant nutritional value for humans, as they are rich in essential fatty acids such as linoleic and linolenic, and also contain tocopherol [5], which helps to improve physiological processes in the body [6]. Nonetheless, the nutrient composition of acorns exhibits considerable variation contingent upon oak species and geographical location.

Another potential use for acorns is in the energy sector. They have a high potential for biofuel production, which is a promising step towards sustainable development and energy independence. The oil extracted from acorns can be used to produce biodiesel [7; 8], reducing our dependence on traditional fuel resources and minimizing harmful emissions. Additionally, acorn starch can be used to produce bioethanol [9] and biobutanol [10; 11], which are environmentally friendly alternative energy sources.

Since acorns contain a significant amount of lignin, which is approximately 30 % by weight [12], there is a potential to use them as a raw

material for the production of alternative solid fuels without the use of additional binders. Studies [12] have shown that the cork oak acorns (*Quercus suber*) are an effective raw material for this purpose. However, this study does not provide data on the higher calorific value and ash content of alternative solid fuels from acorns.

Considering the positive results of previous studies of similar renewable plant materials [13], it is reasonable to study the possibility of creating an alternative solid fuel from acorns of the common oak (*Quercus robur*), which is widespread in Ukraine, and that was the purpose of this study.

Experimental part

The objects of research were the common oak acorns (*Quercus robur*) gathered in the park area in Lviv, Ukraine (Fig. 1). The acorn shells and acorn cups were initially crushed using a laboratory electric mill and then dried in a laboratory installation by the filtration drying method as described in [14]. This method was chosen considering its advantages [14] for increasing the shelf life of raw materials and the possibility of forming solid fuel samples [15; 16].



Fig. 1. The common oak (*Quercus robur*) acorns

The briquettes were formed from experimental mixtures using a 150 °C mold temperature, 100 kgf/cm² pressure, and 60 sec duration on a P474A hydraulic press and based on recommendations [17].

The combustion calorimetric method was used to determine three main characteristics of the studied material: residual moisture content, ash content, and higher calorific value in accordance with the State Standards of Ukraine

[18–20]. Calorimetric studies to determine the higher calorific value were performed using a precision combustion calorimeter B-08-MA with an isothermal shell (± 0.003 K) and a static calorimetric bomb. The energy equivalent of the calorimetric system ($W=10348\pm 10$ J/V) was determined with an accuracy of $\pm 0.09\%$ by burning the reference K-1 benzoic acid, the content of the main component of which reached $99.995\pm 0.01\%$ mol. The heat of combustion of benzoic acid ($\Delta_c U$), taking into account the Jessup factor, was -26434.4 J/g.

The material samples were burned in terylene ampoules. The terylene ampoule was tied with a cotton thread and placed in a platinum cup. The inflammation of the sample during the experiment was initiated by discharging capacitors through a platinum wire, which ignited the cotton thread. The initial pressure of oxygen pre-purified from combustible impurities, carbon dioxide, and water was 32 kPa, and the initial temperature of the main period in all experiments was 298 K. The calorific value was determined according to formula (1) [16; 20]:

$$Q = \frac{W \cdot \Delta T - q_{\text{thread}} - q_{\text{ampoule}} - q_{\text{HNO}_3} + q_{\text{soot}}}{m}, \quad (1)$$

where W – the energy equivalent of a calorimetric system;

m – the mass of the substance that was burned during the experiment;

q_{thread} , q_{ampoule} , q_{HNO_3} , q_{soot} – the amount of energy released during the combustion of a cotton thread (16704.2 J/g), a terylene ampoule (22944.2 J/g), the formation of a nitric acid solution (59 J/g) and soot (32800 J/g), respectively;

ΔT – the true temperature rise in the calorimetric experiment.

The ash content of the studied raw materials was determined according to the requirements of

[19], and the residual moisture content was determined according to the method of [18].

Results and their discussion

The crushed plant material of the common oak acorns (Fig. 2) was pre-dried by the filtration drying method from an initial moisture content of 43.37 % wt. to a final moisture content of 4.48 % wt.



Fig. 2. Crushed and dried acorns of the common oak (*Quercus robur*)

Considering the heterogeneity of the composition of the crushed plant material, 3 parallel experiments were conducted to determine the average value of the higher calorific value and ash content of the material under study. The measurement results are shown in Table 1.

Table 1 shows the average values of the higher calorific value of the dried experimental mixture №1 and experimental mixture №2.

Table 1

Results of the experimental determination of the highest calorific value and ash content according to the calorimetry of combustion of experimental mixtures from the common oak acorns (*Quercus robur*)

Test, №	m, g	$\Delta T, V$	q_{thread}, J	q_{HNO_3}, J	q_{soot}, J	q_{ampoule}, J	Q		Ash content, % wt.
							kJ/kg	kcal/kg	
1	0.75181	1.47688	153.3	2.1	58.1	1572.6	18107	4328	0.88
2	0.87114	1.70907	141.7	2.1	98.6	1772.3	18215	4353	0.94
3	0.88123	1.71231	154.4	1.2	142	1695.6	18168	4342	0.98
The average value:							18163	4341	0.93

Comparing the obtained experimental data on the calorimetry of combustion of prototypes of unformed plant material, it is clear that the values of the higher calorific value are slightly higher

than the values for energy willow and miscanthus, which are widely used in the industrial production of solid fuel briquettes from renewable plant material [21; 22]. For

comparison, we also present similar values for the plant material studied earlier [13] (Table 2).

Table 2

The value of the higher calorific value of the study objects and their analogues

Raw materials of plant origin	Dried kernels of horse chestnut seeds	Dried acorns of the common oak	Energy willow	Dried kernels and the outer shell of horse chestnut seeds	Miscanthus
Calorific value, kJ/kg	≈ 18351	≈ 18163	≈ 17600	≈ 17549	≈ 17500

Taking into account the experimental data obtained, acorns of the common oak (*Quercus robur*) are a promising raw material for the production of alternative solid fuels as they have a high calorific value (≈18163 kJ/kg) and low ash

content (<1 % wt.) (Table 1). Therefore, the research was continued – briquetted samples of alternative solid fuels were produced and their corresponding studies were performed.



Fig. 3. A briquetted sample of solid fuel obtained from the acorns of the common oak (*Quercus robur*).

The data of the results of the study of the higher calorific value and ash content of briquetted samples from the fruits of common

oak (*Quercus robur*) are given in Table 3. The moisture content of all obtained samples was <1 % wt.

Table 3

Results of experimental determination of the highest calorific value and ash content according to the calorimetry of combustion of briquetted experimental mixtures samples from acorns of the common oak (*Quercus robur*)

Test, №	m, g	$\Delta T, V$	q_{thread}, J	q_{HNO3}, J	q_{soot}, J	$q_{ampoule}, J$	$Q,$		Ash content, % wt.
							kJ/kg	kcal/kg	
1	0.98351	1.65471	116.6	1.2	104.8	-	17397	4158	1.15
2	1.05626	1.77734	131.1	2.4	143.8	-	17422	4164	1.25
3	1.68586	2.84317	82.4	3.0	109.2	-	17466	4174	1.25
The average value:							17428	4165	1.22

It's worth noting that the higher calorific value of briquetted samples slightly decreases after their formation. This could be due to the release of volatile organic compounds with high calorific value during the pressing process at a temperature of 150 °C. Similar observations have been made in previous studies on the use of coffee production waste for creating alternative solid fuels [23]. Further research and analysis of the gases and vapors generated during the pressing process is required to answer this question.

The obtained data of higher calorific value, ash content and residual moisture content fully comply with the existing requirements of the Swedish standard SS 187120, according to which alternative fuels have to meet the following characteristics: calorific value (>16910 kJ/kg),

ash content (<1.5 %), residual moisture (<10 %), as well as to the German standard DIN 51731 (calorific value (15512÷19515 kJ/kg), ash content (<1.5 %), residual moisture (<12 %) [24].

Conclusions

The results of our research demonstrate the potential use of acorns of the common oak (*Quercus robur*) as plant material for the production of alternative solid fuels. As a result, we obtained ready-to-use samples with a higher calorific value of ~17428 kJ/kg, ash content of ~1.22 % wt. and residual moisture content of <1 % wt.

The production of alternative solid fuels from acorns will improve the environmental situation by replacing traditional fuel resources and may be an option for the rational usage of renewable natural raw materials. In addition, briquettes

made from the acorns of the common oak (*Quercus robur*) do not require any additional binders and meet existing European standards.

An additional advantage is the low cost of the raw material. However, there are still questions about the usage of acorns for energy needs on an industrial scale, as acorns are not common and can be difficult to collect and harvest in the wild.

Author Contributions

OI had the initial idea and conceived the experiments. VA developed methods of analysis of raw material and its filtration drying. RC, VM, and SB prepared the laboratory installation for the crushed acorns filtration drying. OI, RC, VM, and SB gathered the raw materials and performed the acorns drying. OI and RC made solid fuel samples. IS performed calorimetric studies. OI and VA analyzed the experimental results. OI, VA, RC and VM wrote the draft of the article. OI and VA supervised the work.

References

- [1] Tkach, V., Rumiantsev, M., Kobets, O., Luk'yanets, V., Musienko, S. (2019). Ukrainian plain oak forests and their natural regeneration. *Forestry Studies / Metsanduslikud Uurimused*, 71, 17–29. <https://doi.org/10.2478/fsmu-2019-0010>
- [2] Rumiantsev, M., Luk'yanets, V., Musienko, S., Mostepanyuk, A., Obolonyk, I. (2018). Main problems in natural seed regeneration of pedunculate oak (*Quercus robur* L.) stands in Ukraine. *Forestry Studies / Metsanduslikud Uurimused*, 69, 7–23. <https://doi.org/10.2478/fsmu-2018-0008>
- [3] Rumiantsev, M., Kobets, O., Vysotska, N., Luk'yanets, V., Obolonyk, I., Tupchii, O., Bondar, O., Nazarenko, V. (2023). Acorn production of Pedunculate Oak in northeast of Ukraine. *Forestry Studies / Metsanduslikud Uurimused*, 78(1), 14–27. <https://doi.org/10.2478/fsmu-2023-0002>
- [4] Cantos, E., Espiñ, J. C., López-Bote, C. J., De La Hoz, L., Ordóñez, J., Tomás-Barberán, F. A. (2003). Phenolic Compounds and Fatty Acids from Acorns (*Quercus* spp.), the Main Dietary Constituent of Free-Ranged Iberian Pigs. *Journal of Agricultural and Food Chemistry*, 51(21), 6248–6255. <https://doi.org/10.1021/jf030216v>
- [5] Ventanas, S., Ventanas, J., Tovar, J., García, C., Estévez, M. (2007). Extensive feeding versus oleic acid and tocopherol enriched mixed diets for the production of Iberian dry-cured hams: Effect on chemical composition, oxidative status and sensory traits. *Meat Science*, 77(2), 246–256. <https://doi.org/10.1016/j.meatsci.2007.03.010>
- [6] Sales-Campos, H., De Souza, P. R., Peghini, B. C., Silva, J., De Barros Cardoso, C. R. (2013). An overview of the modulatory effects of oleic acid in health and disease. *Mini-reviews in Medicinal Chemistry/Mini-reviews in Medical Chemistry*, 13(2), 201–210. <https://doi.org/10.2174/1389557511313020003>
- [7] Karabaş, H. (2013). Biodiesel production from crude acorn (*Quercus frainetto* L.) kernel oil: An optimisation process using the Taguchi method. *Renewable Energy*, 53, 384–388. <https://doi.org/10.1016/j.renene.2012.12.002>
- [8] Karabaş, H. (2013). The optimum production parameters of methyl ester from acorn kernel oil. *Environmental Progress & Sustainable Energy*, 33(2), 625–628. <https://doi.org/10.1002/ep.11819>
- [9] Chao, B., Liu, R., Zhang, X., Zhang, X., Tan, T. (2017). Tannin extraction pretreatment and very high gravity fermentation of acorn starch for bioethanol production. *Bioresource Technology*, 241, 900–907. <https://doi.org/10.1016/j.biortech.2017.06.026>
- [10] Heidari, F., Asadollahi, M. A., Jeyhanipour, A., Kheyrandish, M., Rismani-Yazdi, H., Karimi, K. (2016). Biobutanol production using unhydrolyzed waste acorn as a novel substrate. *RSC Advances*, 6(11), 9254–9260. <https://doi.org/10.1039/c5ra23941a>
- [11] Sasaki, C., Kushiki, Y., Asada, C., Nakamura, Y. (2014). Acetone–butanol–ethanol production by separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF) methods using acorns and wood chips of *Quercus acutissima* as a carbon source. *Industrial Crops and Products*, 62, 286–292. <https://doi.org/10.1016/j.indcrop.2014.08.049>
- [12] Allouch, M., Alami, M., Boukhli, F. (2015). Production of fuel friquettes from acorn shells and acorn cups. *2015 3rd International Renewable and Sustainable Energy Conference (IRSEC)*. <https://doi.org/10.1109/irsec.2015.7455026>
- [13] Ivashchuk, O. S., Atamanyuk, V. M., Chyzhovych, R. A., Manastyrska, V. A., Barabakh, S. A., Sobechko, I. B. (2024). Research of solid fuel production from horse chestnut seeds. *Journal of Chemistry and Technologies*, 32(1), 131–137. <https://doi.org/10.15421/jchemtech.v32i1.291068>
- [14] Ivashchuk, O., Atamanyuk, V., Chyzhovych, R., Manastyrska, V., Barabakh, S., Hnativ, Z. (2024). Kinetic regularities of the filtration drying of barley brewer's spent grain. *Chemistry & Chemical Technology*, 18(1), 66–75. <https://doi.org/10.23939/chcht18.01.066>
- [15] Ivashchuk, O. S., Atamanyuk, V. M., Chyzhovych, R. A., Kiiaieva, S. S., Duleba, V. P., Sobechko, I. B. (2022). Research of solid fuel briquettes obtaining from brewer's spent grain. *Journal of Chemistry and Technologies*, 30(2), 216–221. <https://doi.org/10.15421/jchemtech.v30i2.256749>
- [16] Ivashchuk, O. S., Atamanyuk, V. M., Chyzhovych, R. A., Kiiaieva, S. S., Zhrebetskyi, R. R., Sobechko, I. B. (2022). Preparation of an alternate solid fuel from alcohol distillery stillage. *Voprosy Khimii i Khimicheskoi Tekhnologii*, (1), 54–59. <https://doi.org/10.32434/0321-4095-2022-140-1-54-59>
- [17] Ivashchuk, O. S., Atamanyuk, V. M., Chyzhovych, R. A., Manastyrska, V. A., Sobechko, I. B. (2023). Using of barley bran in the production of alternative solid fuel from coffee production waste. *Journal of Chemistry and Technologies*, 31(2), 318–324. <https://doi.org/10.15421/jchemtech.v31i2.274932>
- [18] State Standart of Ukraine [Solid biofuels. Determination of moisture content. Drying method in a drying oven. Total moisture]. (DSTU EN 14774-2:2013). (2013). (In Ukrainian).

- [19] State Standart of Ukraine [Solid biofuels. Method for determination of ash content]. (DSTU ISO 18122:2017). (2017). (in Ukrainian)
- [20] State Standart of Ukraine [Solid biofuels. Method for determining the calorific value" [Biopalyvo tverde. Metod vyznachennia teplotvirnoyi zdatnosti] (DSTU EN 14918:2016). (2016). (in Ukrainian)
- [21] Khivrych, O. B., Kvak, V. M., Kas'kiv, V. V., Mamajsur, V. V., Makarenko, A. S. (2011). Energetychni roslyny yak alternatyva tradycijnym vydam palyva [Energy plants as an alternative to traditional fuels]. *Agrobiologiya*, 6, 153–156 (in Ukrainian). http://nbuv.gov.ua/UJRN/agr_2011_6_39
- [22] Malyovanyi, M.S., Bat', R.Y. (2012). [Fuels pelleting]. *Eastern-European Journal of Enterprise Technologies*, 5/8(59), 10–14. (In Ukrainian) <https://doi.org/10.15587/1729-4061.2012.4599>
- [23] Ivashchuk, O. S., Atamanyuk, V. M., Chyzhovych, R. A., Sobechko, I. B. (2022). Using coffee production waste as a raw material for solid fuel. *Journal of Chemistry and Technologies*, 30(4), 588–594. <https://doi.org/10.15421/jchemtech.v30i4.265116>
- [24] García-Maraver, A., Popov, V., & Zamorano, M. (2011). A review of European standards for Pellet Quality. *Renewable Energy*, 36(12), 3537–3540. <https://doi.org/10.1016/j.renene.2011.05.013>