RAPESEED STALKS: AN UNTAPPED RESOURCE FOR INDUSTRIAL CHEMICAL COMPOUNDS

TULPINILE DE RAPIȚĂ: O RESURSĂ NEEXPLORATĂ PENTRU OBȚINEREA DE COMPUȘI CHIMICI LA NIVEL INDUSTRIAL

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Abstract. *Rapeseed, stands as a versatile crop cultivated worldwide for its seeds, which are rich in oil and protein. Traditionally recognized for its contributions to the agri-food industry and biofuel production, rapeseed's value extends beyond its seeds to its often-overlooked stalks. In recent years, research efforts have intensified to explore the chemical valorization of rapeseed stalks, recognizing their untapped potential as an abundant and valuable biomass resource. By overcoming technical challenges and optimizing valorization pathways, researchers can unlock the full potential of rapeseed stalks, contributing to the transition towards a bio-based economy and addressing environmental and economic challenges in agriculture and chemical industry.*
Keywords: *rapeseed stalks, nonwood resources, pulp, cellulose, fibers*.

Rezumat. *Rapița este o specie polivalentă, cultivată în întreaga lume pentru semințele sale, bogate în ulei și proteine. Recunoscută în mod tradițional pentru contribuțiile sale la industria agroalimentară și la producția de biocombustibili, valoarea culturii de rapiță se extinde dincolo de semințele sale și la tulpinile sale, adesea ignorate. În ultimii ani, eforturile de cercetare s-au intensificat pentru a investiga valorificarea chimică a tulpinilor de rapiță, recunoscând potențialul neexploatat al acestora ca resursă de biomasă abundentă și valoroasă. Prin depășirea provocărilor tehnice și prin optimizarea căilor de valorificare, cercetătorii pot debloca întregul potențial al tulpinilor de rapiță, contribuind la tranziția către bioeconomie și abordând provocările economice și de mediu din agricultură și din industria chimică.*
Cuvinte cheie: *tulpini de rapiță, resurse nelemnoase, celuloză, fibre celulozice*

INTRODUCTION

Rapeseed, a member of the *Brassicaceae* family, known scientifically as *Brassica napus*, is a common crop cultivated extensively for its oil-rich seeds, which serve as raw material for vegetable oil extraction and a source a protein meal. (Tofănică, 2019). Beyond its primary use, rapeseed has been gaining attention for its potential in various industrial applications. Typically, the plant's stalks, considered agricultural waste, present a rich source of lignocellulosic biomass. (Puițel *et al.,* 2011). Thus, these stalks have far greater potential for value-

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added processes, despite traditionally being underutilized for low-value applications such as animal bedding or field mulch. (Tofănică *et al,* 2012; Ungureanu *et al,* 2022).

The successful valorization of rapeseed stalks can yield a variety of valuable products with diverse applications. Pulping is a process that converts lignocellulosic materials into a mass of individual fibers, which can then be used as biomaterials. Thermochemical conversion, such as pyrolysis, is a process that transforms organic materials into useful products through the application of heat. Fermentable sugars obtained from enzymatic hydrolysis can be fermented into biofuels, biochemicals, or bioplastics. The solid residues from the bioethanol production process can be used to adsorb heavy metals from wastewater, offering a high-capacity, low-cost solution for water purification. Bio-oils derived from thermochemical conversion processes can serve as renewable fuels or chemical feedstocks. Additionally, lignin-rich residues can be used for energy generation or further processed into value-added products such as adhesives or carbon fibers. (Măluțan *et al.,* 2017; Puițel *et al.,* 2020).

To aim of the current manuscript is to explore and highlight the potential of rapeseed stalks as a significant source of industrial chemical compounds, thereby promoting the use of sustainable and renewable resources in industry.

MATERIAL AND METHOD

The following materials have been used:

- The rapeseed stalks, harvested from Vaslui, Romania, were carefully selected to ensure they were free of leaves, roots and dirt. After being air-dried and stored in a dry location, the stems were manually cut into 3 - 5 cm pieces in preparation for chemical analysis and pulping. The reported results are based on the oven-dry weight of the samples.

- White liquor needed for soda pulping was prepared by dissolving solid sodium hydroxide in demineralised water. All chemicals were analytical grade.

Work procedure*:*

- Chemical analysis of raw materials were performed according to the following standard methods: TAPPI T204 om - 88 Solvent extractives of wood and pulp; TAPPI T207 om - 88 - Water solubility of wood and pulp; TAPPI T211 om - 85 Ash in wood and pulp; TAPPI T222 om - 88 Acid - insoluble lignin in wood and pulp; TAPPI T264 om - 88 Preparation of wood for chemical analysis. (Tofănică *et al*, 2011a).

- Pulping was performed in a laboratory rotating batch reactor with a volume of 10 L, equipped with electric heating and automatic temperature control. 300 g of rapeseed stalks (on dry basis) and corresponding white liquor (parameters as seen in Table 3) were used, so that pulping was performed with the desired active alkali charge. The ratio of rapeseed stalk to cooking liquor was 1:5 (water was added). After reaching 100ºC, the heating rate was realized to reach the cooking temperature in one hour. Cooking time was 60 minutes at maximum temperature. The cooking parameters were selected in order that pulp lignin content being below the fiber liberation point. After digestion, the brown stock was washed thoroughly with water until no color in the resulting water was observed, and screened on a vibratory screen with 0.25 mm slots. (Tofănică *et al,* 2011; 2011b).

RESULTS AND DISCUSSIONS

Chemical analysis of raw materials is important for both fundamental research and practical applications. By understanding the chemical composition of rapeseed stalks, we can confidently explore their potential use in various chemical reactions and processes. This knowledge is crucial in determining the most effective use of rapeseed stalks in industrial processes to ensure optimal performance and efficiency.

The chemical proportion of components and elements in rapeseed stalks significantly influences its properties and potential applications. For instance, the percentage of cellulose, hemicelluloses, and lignin in the stalks can affect its suitability for various industrial processes such as pulping, biofuel production, and biosorbent creation. (Ungureanu *et al,* 2023). For the use of the stalks in energy generation, chemical elements play a crucial role in their use, since the calorific value and the amount of heat produced by the combustion is determined by them.

From an application point of view, the chemical analysis of rapeseed stalks provides valuable insights into its suitability for specific industrial processes. For example, in the pulp and paper industry, rapeseed stalks can be used due to their cellulose content. Understanding the chemical properties of rapeseed stalks can help in the development of more efficient, sustainable processes. Thus, the chemical analysis of rapeseed stalks plays a vital role in its industrial application, contributing to the advancement of various sectors. Therefore, accurate determination of these proportions is essential in predicting and controlling the behavior of the material in various conditions.

Proximate analysis is a useful method to determine the energetic values of biomass samples. Rapeseed stalks have a significant energetic value. The gross energy of rapeseed is reported to be between 18.60-19.79 MJ/kg (approximately 4470 to 4730 kcal/kg), where the exact energetic value can vary depending on the specific variety of rapeseed and the processing method used. This energy comes from the main chemical components: volatile matter and fixed carbon, that contribute to its energy content. Volatile Matter is essentially a measure of the non-water gases formed from a coal sample during heating. The most common volatile matter in coal is water, carbon dioxide, and sulfur dioxide. As coal rank increases, volatile matter content decreases. Fixed Carbon is a measure of the amount of non-volatile carbon remaining in a coal sample. Fixed carbon is the calculated percentage of material that was lost during the testing for moisture, volatile matter, and ash. Fixed-carbon content increases with rank, and is used to define ranks above medium-volatile coal.

Ultimate analysis determines the elemental composition of a substance, particularly organic compounds. In the context of fuels, the carbon and hydrogen content are of particular importance. The calorific value, or the amount of heat energy released during combustion, is directly related to the carbon and hydrogen content. The greater the percentage of carbon and hydrogen, the higher the quality of the fuel and its calorific value. This is because both carbon and hydrogen are key components in the combustion process, contributing significantly to the energy output.

Table 1

Chemical Characteristics of Rapeseed Stalks (Vassiliev S.V. et al, 2010; 2015)

Component	Rapeseed stalk, % (current research)	Rapeseed stalk, %	$Coal_{minimum}$, %
Proximate analysis, %			
Moisture content	9.1	8.7	0.4
Ash content	5.8	4.3	5
Volatile matter	76.9	70.7	12.2
Fixed carbon	19.5	16.3	17.9
Ultimate analysis, %			
Carbon	46.10	48.5	62.9
Hydrogen	5.8	6.4	3.5
Nitrogen	2	0.5	0.5
Sulphur	0.5	0.10	0.2
Oxygen	39.8	44.5	4.4
Calorific values, MJ/kg			
Net calorific value (LHV)	18.71	14 - 22	16 - 34
Gross calorific value HHV (measured)	19.79	14 - 22	16 - 34
Gross calorific value HHV (calculated)	18.60	14 - 22	16 - 34

Rapeseed stalks consist primarily of cellulose, hemicellulose, and lignin, the three main components of lignocellulosic biomass. Cellulose, a linear polymer of glucose units, provides structural integrity to plant cell walls. Hemicellulose, a heterogeneous polysaccharide, complements cellulose with its branched structure and diverse monosaccharide composition. Lignin, a complex aromatic polymer, confers rigidity to the cell wall matrix. (Ungureanu, 2011).

Together, these components form a matrix that can be broken down and valorized through various chemical processes. Despite its promising chemical composition, rapeseed stalks present several challenges to effective valorization. Lignocellulosic biomass, including rapeseed stalks, is recalcitrant, requiring energy-intensive processes to break down its complex structure. Additionally, the presence of lignin poses challenges in accessing and extracting the cellulose and hemicellulose fractions. Furthermore, the economics of biomass valorization must be carefully considered to ensure the viability and sustainability of the process.

Table 2

Chemical Composition of Rapeseed Stalk

Component	Whole stalk, %	Depithed stalks, %	Fibers, %
Cellulose	40	42	60
Pentosans	23	22	14
Holocellulose	72	75	87
Lignin	21	20	5
Extractives	7	7	2
Ash	6	2	5

Pulping conditions and pulp yields obtained are given in table 3. Depending on pulping conditions, total yields vary between 39 - 45 %. In all processes, pulp total yields decreased with increasing alkali charge. This finding could be explained by the advance of delignification, which reduces the total yield, because of the dissolution of lignin in pulping liquor, and on the degradation and solubilization of other components from plant tissue - especially the hemicelluloses.

In pulping for every 2 % alkali charge, the total pulp yield drop less than a point. At 18 - 20 % alkali charge, processes had similar fiber yields, with limited unscreened fraction. Therefore pulping is reached to the residual stage and should not exceed this value of alkali charge, because further increase with 2 % will only decrease total pulping yield by the disolution of the componnts.

Table 3

Pulping conditions and yields obtained in Soda - AQ pulping experiments

Sample	Alkali charge, %	Temperature, °C	Fibers yield, %	Rejected, %	Total yield, %
RS1	16	160	28	16	45
RS2	16	170	31	8	40
RS3	18	160	38	3	41
RS4	18	170	38	1	41
RS5	20	150	34	7	41
RS6	20	160	40	1	40
RS7	20	170	39	0	39

From the delignification point oif view, the process proceeded quickly with increasing the alkali charge, due to the rapid dissolution of lignin in the cooking liquor. For every 2 % alkali charge, the lignin content droped 25 % and at 4 % differences in alkali charge, the gap between pulp samples reaches 50 % in kappa number units. The results have shown that the delignification rate increase by increasing the sodium hydroxide charge, delignification being extended as proven from the low kappa number of the cellulose fibers.

CONCLUSIONS

1. In terms of energy content, the carbon and hydrogen content of the biomass are of particular importance. Both carbon and hydrogen are key components in combustion processes, contributing significantly to the energy output. The higher the percentage of carbon and hydrogen in the biomass, the higher its calorific value.

2. The chemical composition of rapeseed stalks includes cellulose, lignin, hemicelluloses, pentosan, and ash. These components have various industrial applications, including the production of bioenergy, biofuels, biomaterials, and papermaking products.

3. Several pathways exist for the chemical valorization of rapeseed stalks, each offering unique advantages and challenges. These pathways include thermochemical conversion (pulping, pyrolysis, gasification), chemical pretreatment followed by fermentation, biosorbent, soil amendment, etc.

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