MICROWAVE PRE-TREATED WHEAT STRAW PELLETS AS ADDITIVE FOR ACTIVATION OF THERMAL DECOMPOSITION OF BIOMASS BLENDS

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Abstract. To provide wider use of wheat straw for energy production, microwave (MW) pre-treatment of wheat straw pellets was used to provide active control and improvement of the pellet structure and elemental composition. Wheat straw pellets were pre-treated at the temperature range of 473-573K using an originally designed rotating MW reactor. The effect of MW treatment on the wheat straw structural characteristics, element composition, ash content, and calorific values was analysed. The effect of wheat straw pre-treatment on the thermal decomposition of wheat straw pellets and blends with untreated wood pellets was experimentally studied. The yield of combustible volatiles was estimated varying pre-treatment temperatures and the mass fraction of pre-treated pellets in blends. The joint measurements of the weight loss rate of the fuel blends and the yield of combustible volatiles showed that MW pre-treatment of wheat straw pellets enhances the weight loss of blends up to 23% and the yield of combustible volatiles up to 400%. The results of the experimental study suggest that MW pre-treatment of wheat straw pellets can be used as a tool to provide effective control of the thermal decomposition of fuel blends.

Keywords: renewable fuels, fuel blends, optimal composition, microwave, pre-treatment regimes.

Introduction

Because of large quantities of renewable energy source - agriculture residues (wheat or rape straw) there is a growing interest about the possibility of their wider use to produce cheap and clean energy, to replace fossil fuels and to control global warming, thus meeting the EU requirements to limit the use of fossil fuels for energy production [1].

However, the efficient use of agriculture residues requires solutions that allow to improve the main characteristics of their thermo-chemical conversion by increasing the heating values of straw and by limiting the yield of harmful emissions and ash formation during the energy production. Partial improvement of the main characteristics of these renewable energy sources can be achieved by briquetting and granulating, which allows to stabilize thermo-chemical conversion and to increase the calorific value of straw.

For further improvement of wheat straw applicability for energy production microwave (MW) pre-treatment of straw pellets is suggested, which causes changes in the structural, chemical and elemental composition [2; 3]. It leads to increased reactivity of pre-treated straw and enhanced rate of thermal decomposition, providing a higher yield of volatiles (H_2, CO, CH_4, CO_2) during the thermal decomposition [4; 5]. Besides, the results of preliminary research suggest that an additional improvement of wheat straw applicability for energy production can be achieved using blends of selectively MW pre-treated wheat straw with raw wood pellets [6].

The presented study deals with two biomass fuels – MW pre-treated wheat straw pellets and untreated wood pellets that are blended. The structure of MW pre-treated pellets and characteristics of thermal decomposition, and combustion of blends with wood pellets are analysed to assess the optimal pre-treatment conditions of wheat straw pellets and increase availability of wheat straw for clean and efficient energy production.

Materials and methods

An in-house designed MW reactor was used to study the effect of MW pre-treatment of wheat straw pellets on the development of the thermal decomposition of blends [7]. The pre-treatment consisted of a two-stage process of convective and MW (2.45 GHz) heating in the Ar atmosphere.

The main components of the MW reactor are magnetrons with a power of up to 0.9 kW and a tubular resonator with the coaxial waveguide attached to the bottom of the resonator. 300 g of the wheat straw pellets were loaded into the reactor and then placed inside the resonator providing preliminary convective heating of the pellets up to temperature of 350 K. The convective heating of pellets is followed by dynamic heating up to 450-570 K and then by isothermal MW heating during 20 min at selected temperature while controlling changes in the sample weight and the yields of solid and condensable fractions. Contents of C, H, N were measured in all pellets according to the LVS EN15104:2011 using a Vario MACRO elemental analyser (ELEMENTAR Analysensysteme). Ash content was measured as a residue after ignition at 823 ± 10 K in a Carbolite ELF 11/6B furnace according to the LVS EN 14775:2010 standard. The higher heating value (HHV) of pre-treated wheat straw and raw wood samples was calculated using a regression equation and the data of elemental composition [7]. The porous structure of the pre-treated wheat straw pellets was evaluated from N_2 sorption/desorption isotherms determined in a sorptometer Quntachrome NOVA 4200e. Degassing was performed at room temperature for 120 h. Specific surface area was assessed using Quantachrome software and based on the theories by Brunauer-Emmet-Teller.

An experimental device with average heat capacity up to 5 kW, which combines a gasifier and a combustor, was used to study the thermal decomposition of the blends and the yield of volatiles (CO, H_2, CO_2 C_xH_y). The gasifier was filled with the blends (340-480g), the thermal decomposition of which was initiated using additional heat supply by propane flame flow into the upper part of the biomass layer. A primary air supply below the layer of the biomass blend at the average air supply rate 40 l·min^{-1} was used. The thermal decomposition of the selectively activated blends produces the axial flow of volatiles, which was injected into the combustor, attached to the upper part of the gasifier. The effect MW pre-treatment on the thermal decomposition and the yield of volatiles was studied for two pre-treatment regimes: T_{mw} = 473 K and T_{mw} = 548 K. The mass fraction of pre-treated wheat straw pellets in the blends was varied in the range from 15% to 60%. Measurements of thermal decomposition characteristics of blends: yield of volatiles during gasification, kinetics of the weight loss rate and composition of emissions were done using the Testo 350 gas analyser, thermocouples, and calorimetric measurements and are described in detail in [8].

Results and discussion

In Fig. 1 – a measurements of the weight loss of the wheat straw pellets during MW pre-treatment are shown. It can be observed that the weight loss of pellets can be approximated using an exponential function (R^2 = 0.99), suggesting that wheat straw thermal degradation during MW pre-treatment can be expressed as a first order Arrhenius reaction rate. According to [7], the reaction rate, activation energy and pre-exponential frequency factor are influenced by the elemental composition, surface area and porosity of wheat straw pellets. Fig. 1– b shows that the weight loss of pellets starts with a release of moisture, which predominately occurs at $T < 440$ K [9] and is followed by the partial thermal degradation of lignocellulosic pellets of wheat straw at $T > 500$ K, then decomposition of hemicellulose and lignin increases the relative content of carbon, while decreasing the oxygen content [10].

In Fig. 1 – c increase of the surface area and porosity of wheat straw pellets during MW pre-treatment can be observed and approximated with a linear function on their weight loss. Apparently, it can be related to the conversion rate of pellets increasing the yield of gas and solid products, while decreasing the liquid yield [4]. In accordance with [11], the reason for increasing the specific surface area versus the degree of conversion may be due to the development of active sites during structural conversion of pellets. As a result, reactivity of pre-treated pellets is increased responsible for variations of Arrhenius reaction rate and the rate constants of reactions during MW pre-treatment of pellets [4; 11]. Estimation of the HHV of pre-treated straw pellets and blends shown in Fig. 1 – d confirms that an increase of the carbon content in pre-treated wheat straw pellets (Fig. 1 – b) correlates with an increase of HHV of pre-treated straw pellets up to ca. 26 MJ·kg^{-1}. At temperatures of MW pre-treatment (T = 548 K) the heating value of blends with pre-treated wheat straw pellets exceeds the heating value of raw wood pellets ca. 20 MJ·kg^{-1}.

The effect of MW pre-treatment on variations of the pellet structure, elemental composition, and heating value are the main factors that influence their reactivity in thermal decomposition reactions. In Fig. 2 – a, b it is shown that increasing the pre-treatment temperature and mass fraction of wheat straw pellets in blends results in a faster weight loss of the blends decreasing the duration of their thermal conversion (Fig. 2 – c).

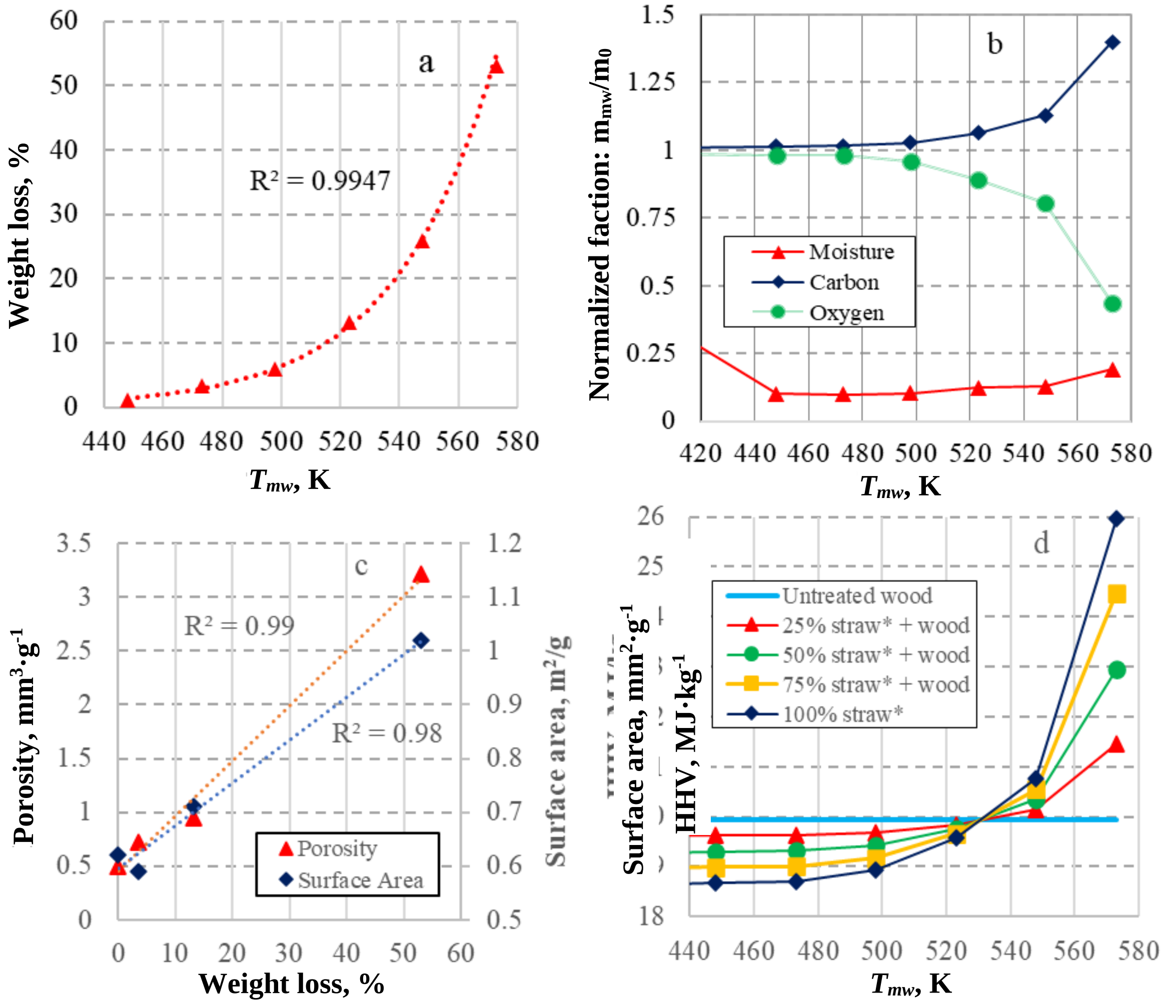

Fig. 1. **Effect of wheat straw pellet pre-treatment on:** a – weight loss; b – normalized elemental composition; c – porosity, surface area; d – HHV of blends with pre-treated straw and untreated wood as reference

In Fig. 2 – d it is shown that the blends of untreated wheat straw with wood pellets dominate a decrease of the weight loss rate as the mass fraction of raw wheat straw pellets in blends increases, which is mainly caused by a decrease in the calorific value of the blends, if the mass fraction of straw pellets in the blend is increased, as it follows from Fig. 1 – d. The deviation from linearity of the average value of the weight loss rate by increasing the mass fraction of straw in the blend suggests the influence of the difference of the chemical composition of pellets. In accordance with the data in [9], wheat straw pellets have higher content of hemicellulose in biomass (≈ 28%), if compared with wood pellets (≈ 22.7%), while lower contents of cellulose (35.4%) and lignin (16.5%), if compared with wood (respectively 43.2% and 28.5%). The average weight loss rate of activated blends tends to decrease increasing the mass fraction of pre-treated straw in the blends up to 40-50% and starts to increase, if the mass fraction of pre-treated straw in the blends exceeds 50% (Fig. 2-d), when correlating increase of the heating value of the blends is observed (Fig. 1– d).

Kinetic study of the yield of combustible volatiles is shown in Fig. 3- a, b. Comparing the yield of CO at thermal decomposition of pre-treated pellets of straw, untreated pellets of wood and blends of pre-treated pellets, it can be concluded that an addition of pre-treated wheat straw pellets to raw wood pellets enhances the yield of combustible volatiles CO during the primary stage of the thermal decomposition (t < 1000 s), while reduces the yield of CO during the end stage of char conversion. This suggests that blending of pre-treated wheat straw pellets with raw wood pellets enhances the thermal interaction between the components. Increasing the temperature of MW pre-treatment and the mass fraction of straw pellets in the fuel blends (Fig. 3 –b) correlate with an increase of the average yield of CO (Fig. 3 – c), confirming the higher reactivity of MW pre-treated wheat straw in reactions of thermal oxidative conversion and therefore the ability to activate the thermal decomposition of the blends containing less reactive biofuel.

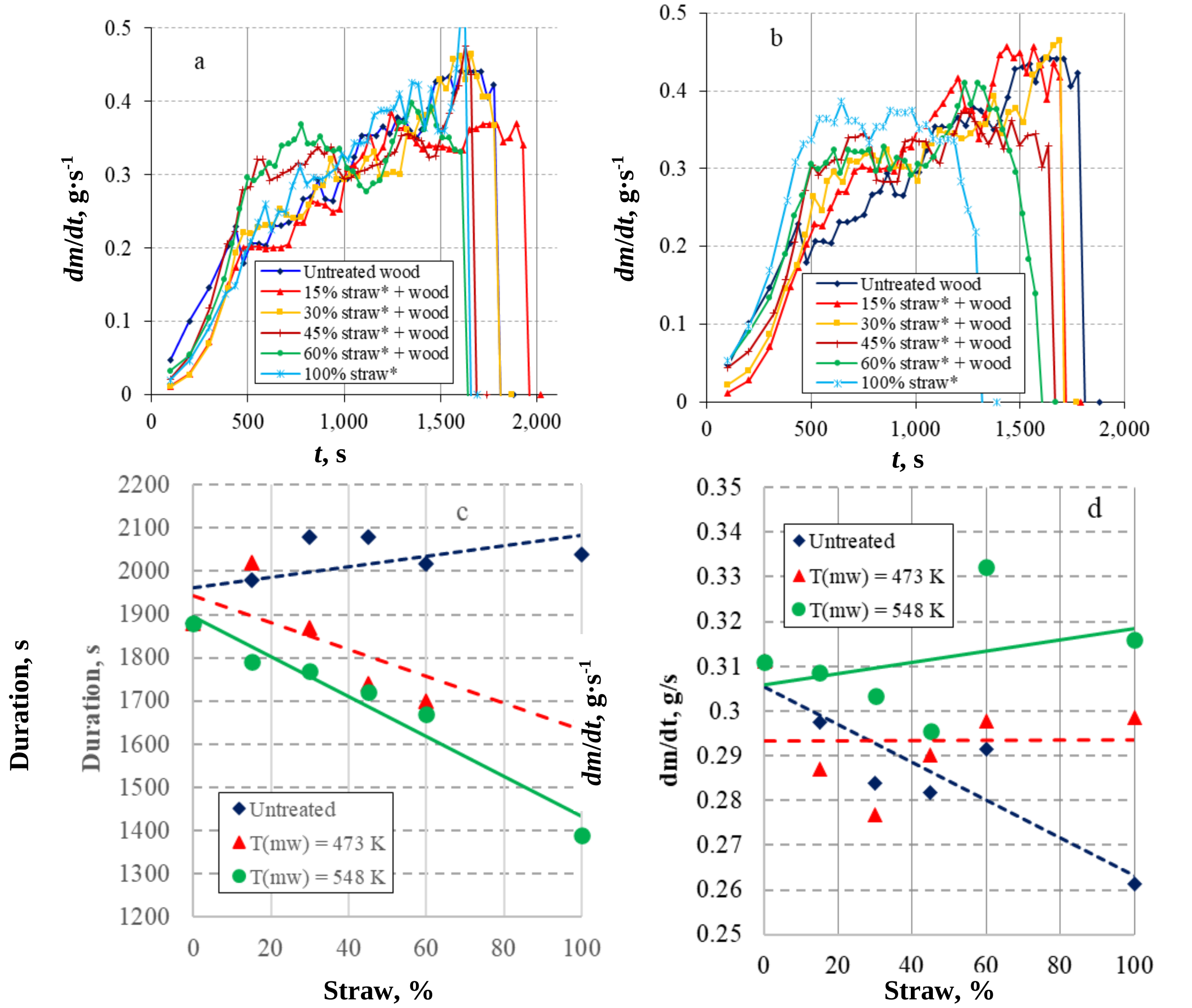

Fig. 2. **Effect of variations MW pre-treatment temperature and mass fraction of pre-treated wheat straw pellets in blends with raw wood pellets on:** a – weight loss kinetics (T = 473 K); b – weight loss kinetics (T = 548 K); c – duration of the thermal decomposition; d – average values of the weight loss rate

The yield of CO_2 for both regimes of MW pre-treatment tends to decrease to the minimum value, which corresponds to mass fraction of pre-treated wheat straw pellets in the blends 40-50% and tends to increase increasing the mass fraction of pre-treated straw pellets in the blends above 50-60%. The decrease of the CO_2 yield to its minimum value during thermal decomposition of the blends is mainly related to the enhanced destruction of wheat straw hemicellulose during the MW pre-treatment of pellets, thus limiting the yield of CO_2 during the thermal decomposition of pre-treated wheat straw. This is evidenced by the enhanced weight loss of wheat straw pellets during the pre-treatment process (up to 50%), which significantly exceeds the moisture content in wheat straw pellets (10.2%) in raw wheat straw pellets and, therefore, suggests the enhanced thermal decomposition of hemicellulose responsible for the enhanced yield of CO_2 [10].

The subsequent increase in the yield of CO_2 increasing the mass fraction of pre-treated straw pellets in the blends above 50-60% can be related to the enhanced thermal interaction of the blend components, which is determined by variation of the porosity, surface area and the heating value of pre-treated wheat straw pellets (Fig. 1 – c, d), increasing their reactivity, intensifying the thermal interaction of the blend components and the thermal decomposition of wood pellets.

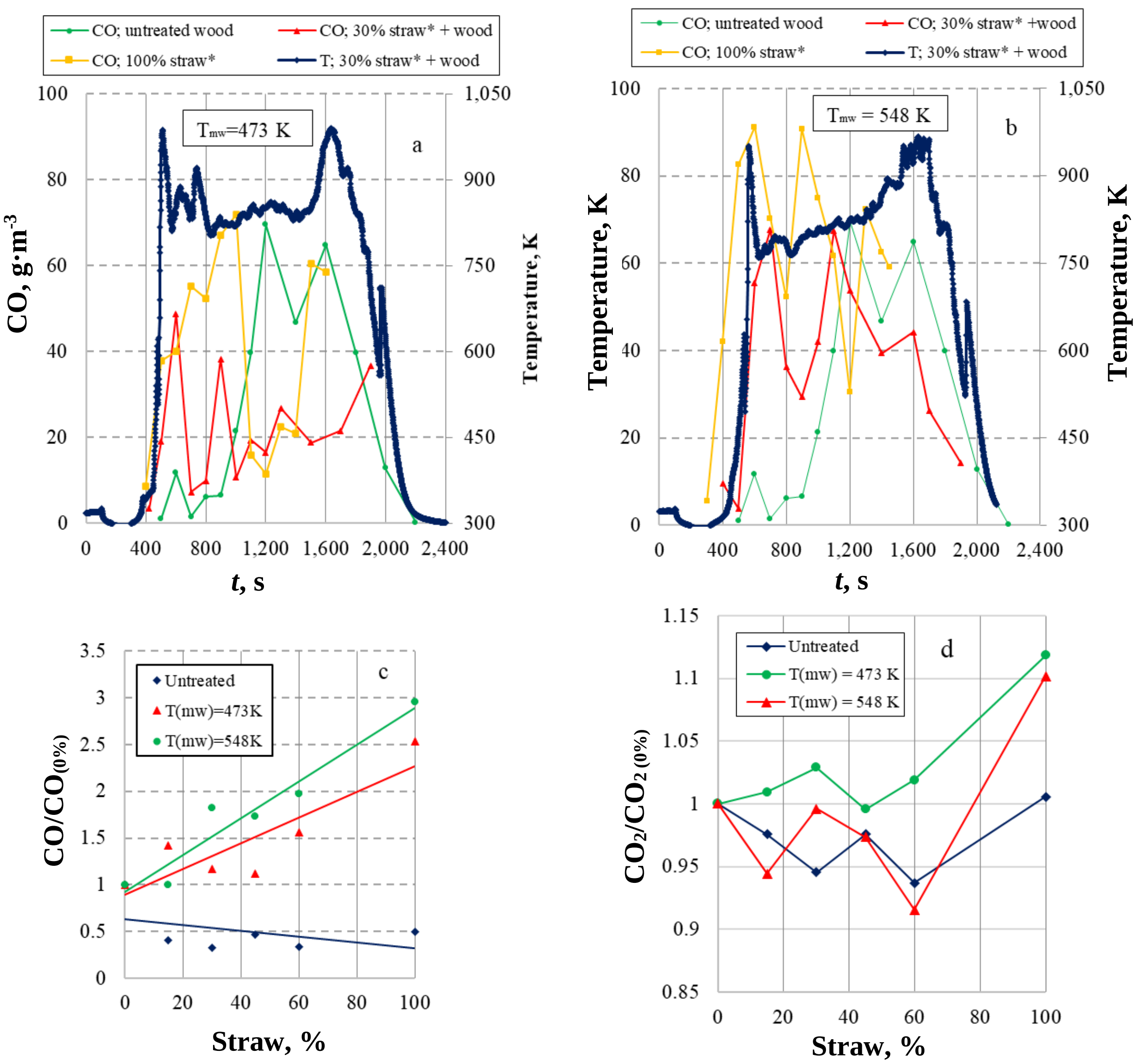

Fig. 3. **Effect of variations of MW pre-treatment temperature and mass fraction of pre-treated wheat straw pellets in blends on:** a – kinetics of the yield of volatiles T_{mw} = 473 K; b – kinetics of the yield of volatiles T_{mw} = 548K; c, d – normalized average values of volatiles

Conclusions

In this experimental study it has been found that the MW pre-treatment of wheat straw pellets results in complex variations of their structure, elemental and chemical composition. As the temperature of wheat straw MW pre-treatment increases, the weight loss, the heating value and the reactivity of pellets also increase.

The increased reactivity and heating value of MW pre-treated wheat straw pellets enhances the thermal interaction between the components determining faster thermal decomposition of blends and the yield of volatiles (CO), decreasing the duration of the blend's thermal decomposition by about 400-500 s. The enhanced yield of volatiles dominates during the primary stage of the thermal decomposition (t < 1000 s) of activated blends with the limited yield of volatiles during the end stage of char conversion (t > 1000 s).

The yield of volatiles of CO_2 during the thermal decomposition of activated blends suggests that it is strongly influenced by the competitive processes of enhanced thermal destruction of wheat straw hemicellulose during MW pre-treatment of pellets and MW-induced thermal interaction between the components of activated blends, determined by increased reactivity and heating values of the wheat straw pellets. As a result of these competitive processes during the thermal decomposition of activated blends the yield of CO_2 (by 18-20%) decreases to the minimum value, which corresponds to the mass fraction of pre-treated wheat straw in the blends 50-60%.

The results of the experimental study suggest that MW pre-treatment of wheat straw pellets can be used to provide effective control of the thermal decomposition of selectively activated fuel blends with beneficial use of straw as a fuel for energy production.

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