

تحقيق تجريبي في انحلال حراري متحاور سويبين قشر

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الخلاصة

متطلبات موارد بديلة للطاقة. بسبب الإفراط في استخدام الوقود الأحفوري، وموارد الطاقة المتجددة ذات أهمية كبيرة. يمكن أن بسبب الإفراط في استخدام الوقود الأحفوري، بموارد الطاقة المتجددة ذات أهمية كبيرة. يمكن أن يكون أحد موارد بديلة للطاقة نفايات الزراعة أو الكتلة الأحيائية. انحلال حراري الكتلة الحيوية لا تنتج الوقودية بل تنتج أيضا شار الأحيائية والكربون المنشط. في انحلال حراري العمل الحالي من سويبين أنجز قشر في مبيعة مما أدى إلى انحلال حراري سريع. سرير بارتيلسيس كانت قاعدة مع النيتروجين وأبقى على ظروف متحاور. بعد الوقت المحدد لوحظت شرطين مختلفة لتبريد سريع ولا تبريد في الغلة الحيوية- شار والحيوي للنفط. قد استخدمت حجم الجسيمات ميكرومتر 250 للتجارب. وتشكل في انحلال حراري عدد كبير من المواد الوسيطة والمنتجات النهائية. كان عمله توازن مادي ليعرف التطاير إينكوندينسابل لكل تجربة. وحصل 83% بيو-النفط و 16% بيو-شار في 1000 °C. ومع ذلك، استنتاج أن وفقا لمتطلبات المنتج من قشر فول الصويا يمكن الحفاظ على درجة الحرارة من رد فعل.

An experimental investigation on isothermal pyrolysis of soybean husk

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Abstract

Due to overuse of fossil fuels, renewable energy resources are of great importance. One of the alternate energy resources could be the agriculture waste or biomass. Biomass pyrolysis not only produces syngas but also produces bio-char and activated carbon. In the present work, pyrolysis of soybean husk was carried out in a fluidized bed, which resulted in fast pyrolysis. The particles bed was fluidized with nitrogen at isothermal conditions. After a specified time, two different conditions of rapid quenching and without quenching were observed for bio-char and bio-oil yield. 250 μm particle size samples were used in the experiments. A material balance was done to determine the incondensable volatiles for each experiment. 83 % bio-oil and 16 % bio-char were obtained at 1000°C. However, at lower temperatures, more bio-char yields were obtained. Therefore, it can be concluded that according to the requirement of the product from soybean husk (bio-oil or bio-char) pyrolysis temperature can be maintained high or low.

Keywords: bio-char; bio-oil; pyrolysis; quenching; soybean husk.

Introduction

Pyrolysis of waste is one of the best economical ways to produce energy from biomass resources from a wide variety of agricultural wastes, industrial processing residues, municipal wastes, and urban wood residues (Ucar et al., 2008). It has become a necessity to convert alternative fuels in replacement of fossil fuels due to their fast depleting rate and to fulfill the energy requirements of the society. Conversion of biomass to energy has two routes: one is thermochemical and the other is biochemical. The thermochemical process can convert biomass including lignin to energy in the form of bio-gas and bio-oil. Pyrolysis is one of the primary thermochemical conversion methods to convert biomass into valuable chars, bio-oil and bio-gas. On the other hand, biochemical process degrades the biomass slowly and releases the volatiles into the atmosphere (Onay, 2007).

To convert biomass into bio-gas and bio-oil, there has been different apparatus used based on the reaction rate. Bio-oils are generally preferred products because of their high calorific value. The gross calorific value of the bio-oil obtained from rapeseed pyrolysis oil cake, empty fruit bunches, and cashew nut shell is 33, 36, and 40 MJ/kg, respectively (Ucar et al., 2008; Abdullah and Gerhauser, 2008; Das et al., 2004). Optimum conditions of bio-oil yield were obtained by fast pyrolysis of safflower seed in a fixed bed reactor with the following conditions: pyrolytic temperature 600°C, sweeping gas flow rate 100 cm^3/min , and heating rate 300°C/min (Onay, 2007). Rapeseed had been investigated for fixed bed slow and fast pyrolysis to observe the effects of heating rate, pyrolysis temperature, particle size, and sweep gas velocity on the yields of product

(Ozlem et al., 2004). Putun et al. (2005) performed fast pyrolysis of cotton stalk in a fluidized bed in the temperature range of 480-550 °C and 55% of bio-oil yield was observed at 510°C.

Fast pyrolysis of soybean hulls had been observed by Oliveira et al. (2015) and compositions of different bio-oil produced were analysed for their calorific values at temperature between 450 and 750°C. Bio-oil and bio-mass can be produced from different sources like coconut shell, soybean hulls, and soybean cake after extraction of soya oil, rice husk, and many other fruits and vegetable peels. Zheng et al. (2008) utilized cotton stalks to generate bio-oil. The yield of bio-oil first increased, and later it was observed to decrease with increasing temperature. The maximum yield of bio-oil that could be achieved was 55% at 510 °C for cotton stalk.

Guo et al. (2011) used a continuous fluidized bed reactor with a capacity of 5 kg/hr. The operating conditions were pyrolysis temperature (450-550 °C) and gas residence time (less than 1 s). The grounded, air-dried particles of rice husk with size of 0.45 to 1 mm were used in all experiments. Cellulose and lignin contents in rice husk are smaller than those in wood materials. This leads to high ash content in rice husk and less volatile vapours; therefore, the yield of bio-oil was also smaller.

Soybean is the largest growing crop in the state Madhya Pradesh, India. Annually 5×10^5 MT of soybean are processed in India and approximately 1 MT of soya cake and hulls are recovered as biomass. The utilization of soybean husk as a bio-char and bio-oil can provide a good source of energy. In the present work, conversion of biomass into char has been done by thermochemical process. This paper presents a pyrolysis study in a fluidized bed at a range of temperatures from 500 to 1000°C at isothermal conditions. The amount of bio-oil and bio-char generated was accounted for and the effect of quenching on the yield of bio-char and bio-oil was observed.

Experimental

Material and equipment

Soybean husk was obtained from a local soya oil company. Before the experiments, the sample was dried in an oven at 80°C for 3-4 hours to reduce the amount of water present in the husk. Soybean husk was then grinded to fine particles in a ball mill. After grinding, sieving of the ground powder was done using sieve shaker. British standard sieve stack was used to analyse the average particle size. On the sample, which was in the range of 250 µm to 300 µm, pyrolysis of soybean husk was carried out in a fluidized bed kept in a muffle furnace. The furnace was lagged with ceramic wool and hysil blocks for insulation. Heaters are made of 80/20 Nichrome wire, which were uniformly wound on the furnace. This muffle furnace can be operated within temperature range of 0 to 1100°C, which could be controlled using an external PID temperature controller.

Two thermocouples were used to measure the temperature of the actual reaction of pyrolysis and vapours formed at the exit of the bed. Thermocouples were of Cr-Al:K type. The diameter of the bed was 20 mm and the length was 60 mm. The bed was stainless steel. The height of particles without fluidization was kept at 50 mm. The schematic of experimental setup is shown in Figure1. Figure 2 shows the actual picture of setup. The volatiles and gases generated during pyrolysis were cooled in a coiled type glass condenser, which was attached to a stainless tube

of diameter 10 mm up to condenser. The cold water was circulated around the outer shell of the condenser. The temperature of the cold water was monitored and maintained at $10 \pm 2^\circ\text{C}$. A change of product composition was observed in pyrolysis of plastic material and more gummy products were formed in fast cooling; however, intermediates were observed in slow cooling (Khan et al., 2016). The intermediate implies that there are some gummy products formed during slow cooling; however, for good bio-oil, light end products should be formed. That gummy product does not form bio-char, and it is not a good bio-oil. Two condensers were used to cool volatile gases after pyrolysis from a fixed bed to produce bio-oil. Therefore, cooling temperature of volatile gases was maintained at 10°C (Khan et al., 2016).

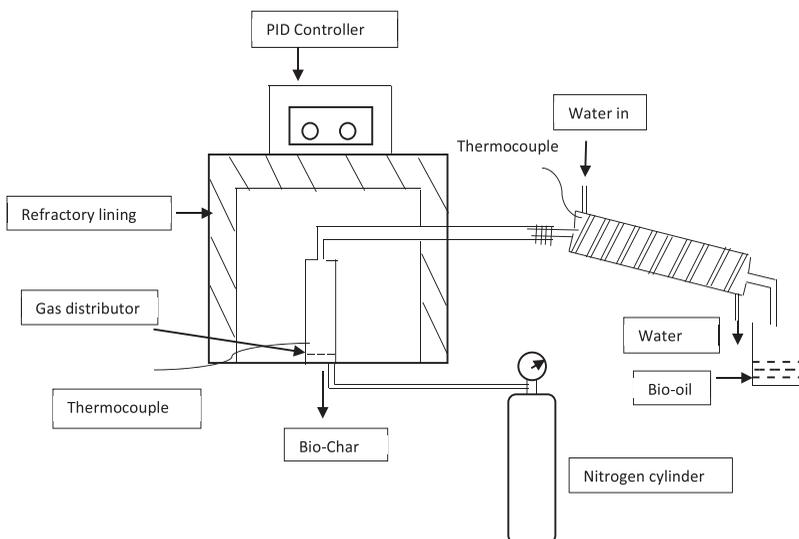


Figure 1. Schematic diagram of experimental setup.



Figure 2. Experimental setup.

Pyrolysis experiments

Pyrolysis experiments were carried out in a fluidized bed, which was kept in a muffle furnace as shown in Figure 1. A bed of soya husk particles was prepared of the mentioned size of predefined weight and was fluidized with nitrogen at 10 LPM. The flow rate of nitrogen in each experiment was kept constant, and this flow rate was sufficient to fluidize the bed up to $\frac{3}{4}$ height of the column. The nitrogen was not preheated. For isothermal conditions, the particles bed was introduced in muffle furnace after achieving the desired temperature. For specified time each experiment was performed individually. After achieving the desired temperature the bed was fluidized and vapors started to evolve as they were approaching to the pyrolysis temperature. After a specified time (30 to 700 sec), the fluidized bed was removed and left to cool down at ambient temperature. To stop the pyrolysis instantly, the bed was dipped in cold water of 5°C, which could stop the pyrolysis instantly. The results with quenching and without quenching were noted separately and analysed. The yields of bio-oil and bio-char as products of pyrolysis were different for both conditions. In order to verify results, experiments were replicated. The temperature of pyrolysis was varied between 500 °C and 1000 °C. The residence time was varied between 30 sec and 270 sec. Table 1 shows the elemental analysis of the feed, which was introduced to the fluidized bed; however, moisture was removed before performing the actual experiments of pyrolysis.

Table 1. Composition and elemental analysis of soybean husk.

Characteristics	Wt (%)
Moisture	11.58
Ash	10.54
C	37.93
H	5.88
N	0.86
S	0.35
O	32.81
Higher heating value (MJ/kg)	15.42

For elemental analysis, moisture estimation was done from soybean husk on 10 gm of grounded sample. It was kept in oven at 105°C for 3 h. After cooling the sample, the weight of sample was measured and loss in weight was considered as moisture. The same sample was kept in the furnace at 550°C to know the ash content for 15 min in the presence of oxygen. The residues left were measured and reported as ash content in Table 1. Other elemental compositions of C, H, N, S, and O were analysed in CHNS(O) analyser (LECO model TRUXCEC). The built-in chromatographic column converts the compounds and elutes them in the form of NO₂, CO₂, SO₂, and H₂O, which are then detected with the help of thermal conductivity detector to calculate the percentage of all elements. The calorific value was measured in Bomb Calorimeter with oxygen as a purge gas. Elemental and composition analyses in Tables 2 and 3 were also performed in similar fashion.

Flash point and fire point were measured in Abel's apparatus where momentary flame was observed for flash point and increasing temperature of 3 -4 °C, continuous flame for 5 sec, was observed. This temperature was considered as fire point. Viscosity of bio-oil was measured in Redwood viscometer and density of bio-oil was measured in pycnometer of 50 ml capacity.

Results and Discussions

Yield of bio-oil with and without quenching

Figure 3 shows the yield of bio-oil with increasing time at different temperatures ranging from 500 to 1000°C. After specified time of pyrolysis the reaction was stopped by quenching of fluidized bed in cold water. Figure 4 represents the yield of bio-oil with increasing time at different temperature without quenching. The operating conditions inside the fluidized bed were kept similar for quenching and without quenching. Vapours generated with both conditions were condensed and accounted for as bio-oil. The yield of bio-oil was 0.5 -1% by weight when there was no quenching. The reason behind this is that the reaction of pyrolysis continues even after removing the fluidized bed from furnace. The stainless steel tube of fluidized bed sustained the temperature for some time after being removed from the furnace.

It is clear from Figures 3 and 4 that as time increases, bio-oil generation increases; however, a plateau is seen after 300 sec where there is no change in the yield of bio-oil at all temperatures studied. The conditions for fast pyrolysis process were studied, namely, dry feedstock (less than 10%), particle size (less than 3 mm), residence times (0.5–2 s), moderate temperatures (400–500 °C), and rapid quenching at the end of the process. It resulted in typical yields of bio-oil, char, and gaseous products of 60–70%, 12–15%, and 13–25%, respectively (Wan et al., 2012).

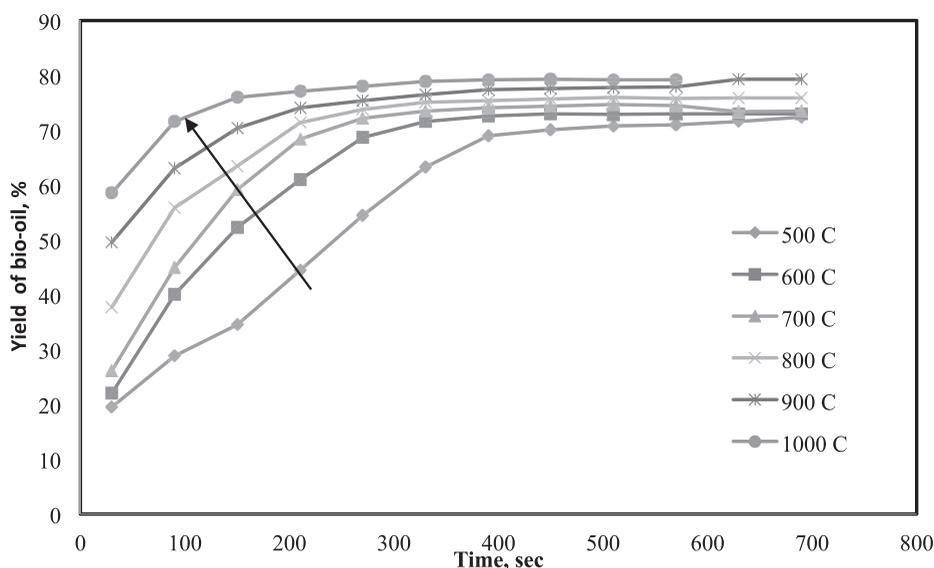


Figure 3. Yield of bio-oil generated at different temperature and increasing time with quenching.

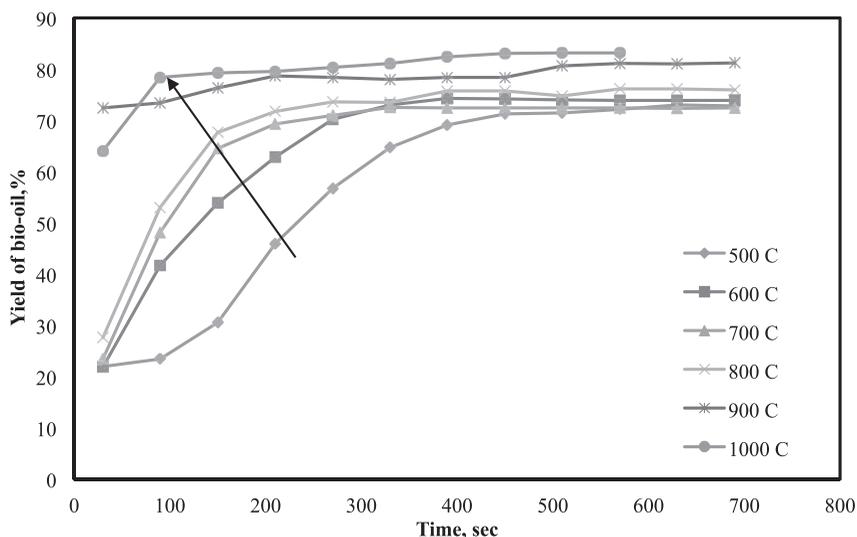


Figure 4. Yield of bio-oil generated at different temperature and increasing time without quenching.

The transition time from increasing to achieving constant weight gain is about 270 seconds at all temperatures. It is shown separately in Figure 5 for quenching and without quenching conditions. It can be noticed that, without quenching, and at 900 and 1000°C, the yield of the bio-oil is 65- 80 % in the time range of 60-120 sec; however, with quenching, it is between 60 and 75%. It should be noted that Ozlem and Kocker (2004) studied the pyrolysis of rapeseed at 30°C/min in fixed bed reactor. Their experiments lead to yields in the range of 41-47 wt % of liquid at 400 -550°C; however, the liquid yields of safflower seed press and soybean cake were found to be 30-33 wt% and 26-30 wt%, respectively (Sensoz and Angin, 2008; Putun et al., 2002).

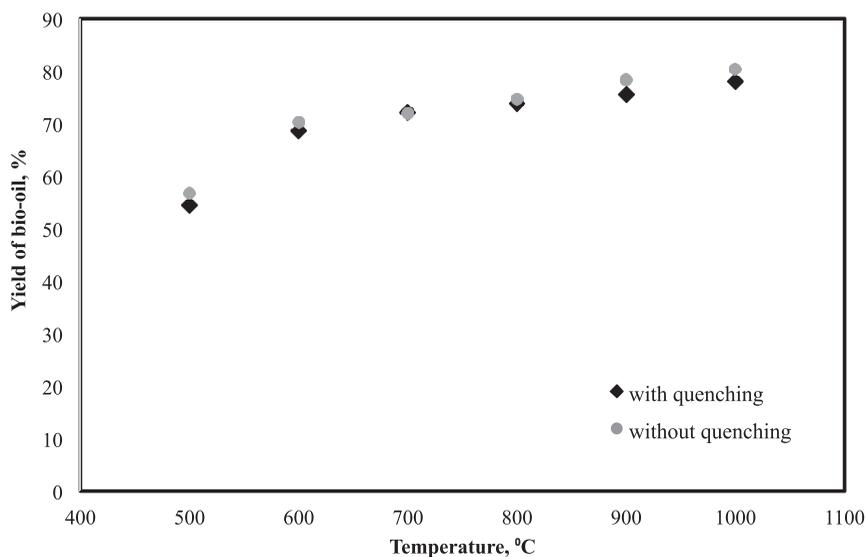


Figure 5. Increase in bio-oil with increasing temperature with and without quenching at 270 sec.

The composition of oil generated at 800°C for 270 seconds was analysed. The results are presented in Table 2. Physical properties of bio-oil were determined. Higher calorific value was presented in Table 2 of bio-oil for soya husk and is comparable with those found by Sundaram and Natarajan (2009) in a fixed bed (38.6 MJ/kg). Bardalai and Mahanta (2016) have achieved only a value of 15.2 MJ/kg due to a higher moisture present in bio-oil produced. Table 2 presents the bio-oil analysis produced at 800°C for 4.5 minutes. It can be emphasized that as the temperature of the isothermal pyrolysis increased, less gaseous products were formed and more bio-oil was produced. Putun et al. (2005) have obtained a H/C ratio of 1.58 for soybean cake pyrolysis, whereas in the present study it was 1.42 for the bio-oil obtained.

Table 2. Properties of bio-oil at 270 seconds at 800°C with quenching.

Properties, elemental (wt %)	Bio-oil
Carbon	32.5
Hydrogen	46.2
Nitrogen	1.8
Oxygen	12.2
Moisture	6.84
Density (kg/m ³)	1080
Viscosity, 40°C (cSt)	32
Flash point (°C)	68
Fire point (°C)	71
Higher heating value (MJ/kg)	37.4

Yield of bio-char with and without quenching

It can be observed from Figures 6 and 7 that the char decreases with the increase in temperature. The amounts of volatiles and gases are increased as the temperature is increased. At higher temperatures, larger molecules of the soybean husk are broken into smaller size particles, which enrich the volatiles. At higher temperatures, cellulose depolymerizes and increases the amount of volatiles and gases.

Figure 6 shows the effect of time at different temperatures of char formation with quenching. The char formation is greater at lower temperatures of 500-700 °C. Similar results without quenching were obtained from Figure 7. If the fluidized bed was not cooled instantly, pyrolysis would continue even after removing the bed from the furnace and volatiles were kept generating; this results in less char formation. After 400 seconds with quenching, 28-30% of char was formed. As a result of no quenching experiments at 500°C, which is the lowest temperature, and at highest temperature 1000°C, the chars obtained were 40% and 10%, respectively.

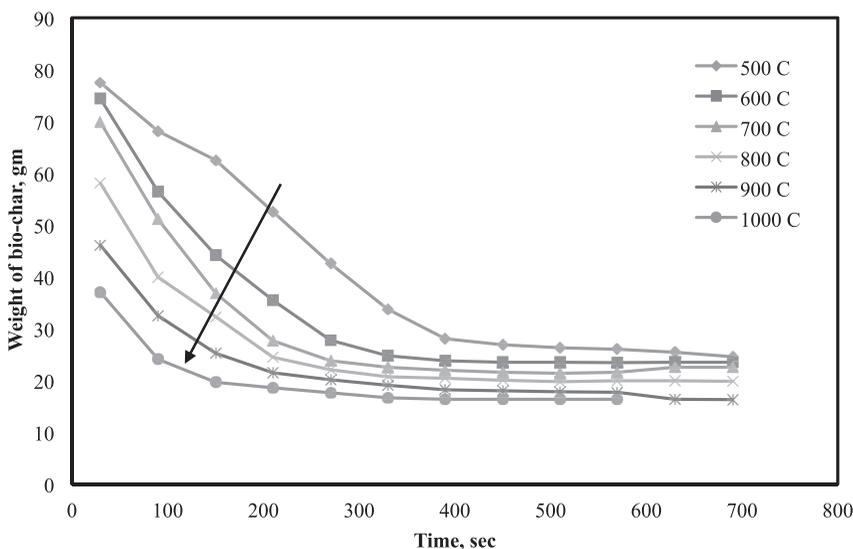


Figure 6. Yield of bio-char with increasing time at different temperature with quenching.

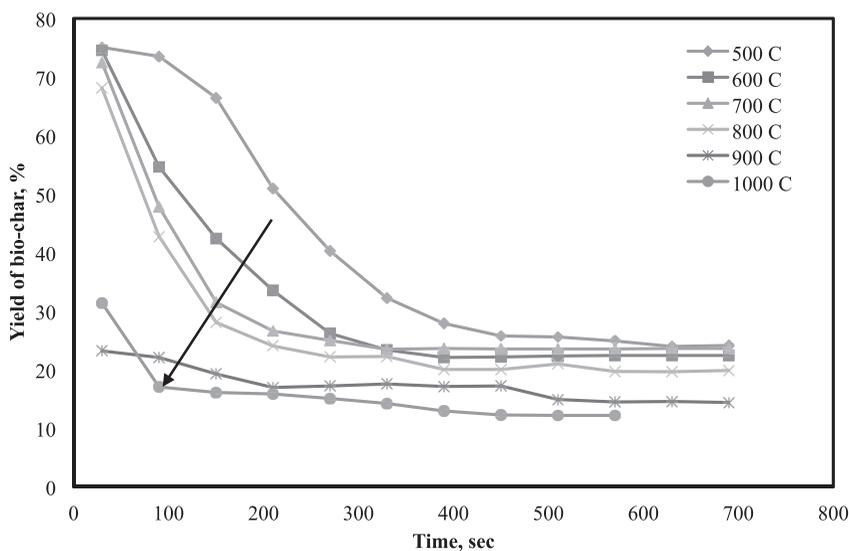


Figure 7. Yield of bio-char with increasing time and different temperature without quenching.

At transition time, decreasing amount of char comes to a constant yield for a particular temperature as seen by the arrow in Figure 7. Every single constant bio-char yield at a particular temperature was plotted in Figure 8. The same figure also shows the effect of quenching and no quenching on the bio-char yield. It can also be observed that the increasing temperature generates more volatiles and less char. The plot was made for pyrolysis at 270 seconds. For constant time at 270 seconds increasing temperature yields only 14 % of bio-char.

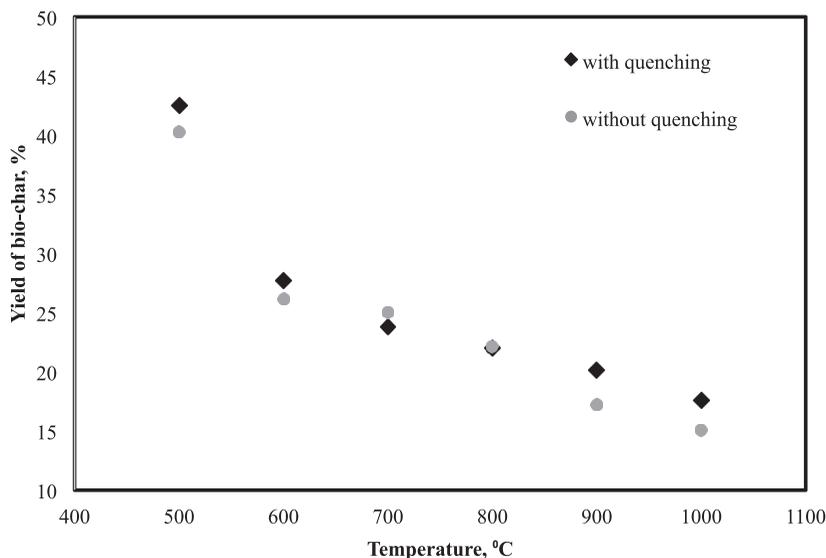


Figure 8. Yield of bio-char at increasing temperature at 270 sec with and without quenching.

The ultimate analysis of bio-char produced by pyrolysis at 800 °C for 270 seconds is shown in Table 3. The calorific value was 21.23 MJ/kg. Similar heating value was obtained by Uzun et al. (2006) for bio-char produced from soybean cake for which the value of heating value was 23.23 MJ/kg. A higher heating value of bioactive biomass was obtained as 29-30 MJ/kg with fast pyrolysis by Miao et al. (2004). The calorific value of other biomass like rice straw, coconut shell, and sugarcane bagasse range between 16 and 22 MJ/kg (Boateng et al., 2007). The composition of bio-char and bio-oil produced is highly dependent on the conditions of pyrolysis. The slow pyrolysis generates more bio-chars than bio-oil; however, for increased amounts of bio-oil fast pyrolysis conditions prevailed.

Table 3. Properties of bio-char at 270 seconds at 800 °C with quenching.

Properties, Elemental (wt %)	Bio-char
Carbon	52.7
Hydrogen	6.4
Nitrogen	6.8
Oxygen	26.6
Moisture	7.3
Ash	4.25
Higher heating value (MJ/kg)	21.23

The total material balance was done for all the experiments, and the final constant yields of bio-char, bio-oil, and incondensable were done at 500 seconds for different temperatures ranging from 500 to 1000 °C. Table 4 presents the material balance and shows that increasing temperatures from 500 to 1000 °C yields 72-83% bio-oil, 24-16% bio-char, and the rest was lost in incondensable vapours, which may contain very light fraction of hydrocarbons that were unable to condense at atmospheric pressure.

Table 4. Yield of bio-char, bio-oil, and the state of being incondensable with quenching and without quenching.

Temp (°C)	Bio-oil		Bio-char		incondensable	
	With quenching (wt %)	Without quenching (wt %)	With quenching (wt %)	Without quenching (wt %)	With quenching (wt %)	Without quenching (wt %)
500	72.42	72.86	24.58	24.14	3	3
600	72.94	73.92	23.46	22.48	3.6	3.6
700	73.44	74.2	22.56	21.5	4	4.3
800	75.94	76.04	19.86	19.76	4.2	4.2
900	79.3	81.02	16.3	14.4	4.4	4.58
1000	79.2	83.2	16.2	12.2	4.6	4.6

Conclusions

In the present study, soybean husk was pyrolysed to produce bio-oil and bio-char at isothermal conditions in a fluidized bed with a constant nitrogen flow rate. Due to fluidized bed, fast reaction of pyrolysis takes place, and even short residence can achieve higher yields of bio-oil and bio-char. Experiments were performed at different temperatures with increasing time from 30 seconds to 700 seconds. Current experiments were also performed at higher temperatures at 800-1000 °C to know the yield of bio-char and bio-oil. The experiments were also performed to determine the effect of rapid quenching and without quenching of the reaction to estimate the yield of bio-oil and bio-char.

It can be concluded from the results that pyrolysis reaction with quenching yields more bio-char; however, without quenching more volatiles and as a result, more bio-oils were obtained. At higher temperatures like 900 and 1000 °C yields of bio-char and bio-oil with increasing time do not vary appreciably and approximately constant yields were obtained. However, 83 % of bio-oil and 16 % of bio-char were obtained at 1000 °C.

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