Co-Pyrolysis of Lignite and Oil Plant Cake Blends

***Yilgin, Melek**+**

Firat University, Chemical Engineering Department, 23279, ELAZIĞ, TURKEY

ABSTRACT: *Although today's fossil fuel reserves have been still considered a long-term energy supply, biomass has received worldwide attention as a cheap and renewable energy source due to the known global environmental impact of fossil fuel usage. Then co-processing of fossil fuels and biomasses to produce substitute liquid fuels is one option to appraise fossil fuel reserves for the economy. In this work, pyrolysis of Soma lignite and an oil plant cake, and their blends of varied proportions in the form of pellets were studied to elucidate the main differences between the behavior of these materials and their blends during fast thermal decomposition carried to convert their valuable products. A special vertical heating chamber, which enabled very fast heating, was used in the experiments conducted at 500-700ºC temperature range. The results showed that these two materials mutually interacted when the cake ratios of the pellets were below 50%. For blends with 75% cake, some interaction was observed only at 700ºC. It is concluded that the interaction between two materials during pyrolysis is affected by the outflow rates of volatiles into the sweeping gas. Maximum liquid yields corresponded to blends containing OPC greater than 75%.*

KEYWORDS: *Lignite; Oil plant cake; Co-pyrolysis; Synergistic effect.*

INTRODUCTION

Although coal is regarded as a long-term fossil fuel for today and future utilization, much attention has been given to the use of wastes and biomasses as renewable raw materials in energy production [1] due to environmental regulations about fossil fuel usage and growing fears of climate change stemming from increasing greenhouse gas emissions. Bioenergy has surpassed oil, coal, and natural gas as the fourth most important primary energy source. Unlike solar and wind energy, which are primarily used to generate electricity, bioenergy development is primarily focused on the production of biofuels that may be utilized for both heat energy and power generation as well as a transportation [2].

The term biomass is used for all organic matter derived from plants. Biomass sources include wood and wood waste, crops and their by-products, municipal solid waste, wastes from food processing, aquatic plants, and algae [3]. Dispersal and seasonal supply may cause increased transportation and storage costs [4]. Biomasses are usually preferred in uniform pellet forms for burning in industrial appliances due to their advantage of high energy density that makes transport, investment for storage, and process feeding costs smaller than non-pellet fuels. Wood pellets are already commercialized and utilization in power plants as well as for residential heating has increased significantly in recent years [5,6]. However, they don't resist water, crumble easily, and are not durable long under moist storage conditions [7].

Pyrolysis has been extensively investigated as a thermochemical conversion process for the conversion of carbonaceous materials into gas, liquid, and chars under controlled process conditions [8]. Coal pyrolysis is a forward-looking process for obtaining liquid fuels and synthetic gases [9]. However, coal is a fuel that is low in hydrogen. Biomass, on the other hand, is one of the H-rich resources. As a result, the H/C ratio in the co-pyrolysis of coal and biomass could be altered, resulting in increased industrial flexibility and efficiency. Furthermore, pyrolysis releases more volatiles from biomass, and biomass-derived hydrogen improves coal conversion during the pyrolysis process. Co-pyrolysis of coal and biomass, as an effective upgrading process, may not only improve coal conversion but also effectively promote the value recycling of biomass [10]. This is why co-pyrolysis of coal and biomass is used to increase crop yield.

Biomass is generally composed of three main components: lignin, cellulose, and hemicellulose. Each component has different pyrolytic behaviors that are likely to start decomposition at a lower temperature (200°C). However, the thermal decomposition of coal usually starts above 350 °C. Therefore, the heating rate is important during the co-pyrolysis of these two materials. Otherwise, the pyrolysis of the biomass ends before the pyrolysis of lignite [11].

Many studies have been conducted on the co-pyrolysis of biomass and coal. The majority of these studies aim to use coal and biomass to produce substitute liquid fuels for oil in high yields. For example, coal-straw and coal-agricultural waste blends pyrolyzed in different systems gave higher liquid yields with increasing biomass ratio [12, 13]. However, the type of reactor has been reported to influence significantly the oil yields and quality [14]. Corn stover-brown coal blends gave higher oil yields with increasing temperature and biomass/coal ratio in microwave-assisted co-pyrolysis between 500-600°C, and some positive synergistic effect on oil yield was also reported at 600°C for 0.33 biomass ratio [15]. Staged catalytic pyrolysis of lignite/straw mixtures indicated some synergetic effects on the chemical composition of liquid pyrolysis products[16]. The volatile release rate of corn stalk-coal blends was reported to be lower than the expected values [17]. Co-pyrolysis of low-rank coal with two microalgae has been reported to result in higher liquid yields than individual materials [18]. Co-pyrolysis of a pre-treated caking bituminous coal with corn stalk was claimed to have a synergistic promoting effect on the formation of H_2, CO_2, and CH_4 components in gas [19]. Thermal gravimetric studies under inert gases have also shown a synergistic effect with some coal/biomass blends [20,21]. In the study in which the pyrolysis properties of Camellia oleifera bark (COS), coal, and their mixture were investigated using TGA and a fixed bed reactor, it was stated that the optimum liquid product yield was obtained from the mixture containing 60% COS at 600 °C in the study was carried out in the fixed bed. In this study, it was also emphasized that the TGA results were different from the fixed bed results and the fixed bed results were the same as the expected values [22]. The pyrolysis properties of four different oil mill wastes were investigated using GC coupled fixed bed reactor and TGA. The char obtained from TGA was higher than that obtained from the fixed bed [23]. Co-pyrolysis properties of white pine and sub-bituminous coal mixture was investigated in TG and free fall reactor. Results from TG show that interactions between blends offer an inhibitory effect on thermal decomposition, resulting in higher-than-expected char yields, while a positive synergy effect on tar production was observed in the free-fall reactor under a higher biomass blending ratio [24]. The results of these studies reveal that the parameters such as coal/biomass ratio, temperature, and type of pyrolysis system are the most important factors determining the synergy between two materials in terms of product quantities, and their composition.

One of the challenges faced by developing countries is an economic appraisal of fossil fuel reserves. Turkey has considerable lignite reserves. Lignite usage as a fuel provides a large fraction of the needs in Turkish energy system and presents the most importantly atmospheric pollution source [25]. Burning lignite as mixtures with proper biomasses or appraising them by converting economically viable products are the options for coping with environmental issues related to lignite utilization in power stations. It is known that solid, liquid, and gas product yields and compositions change due to the synergistic effect during the co-pyrolysis of lignite and biomass. Residue cakes of vegetable oil plants are among the important industrial biomass wastes. They have low hydrogen content compared to most biomasses. Although there are some utilization and appraisal areas of these

residues, no studies have been found on co-pyrolysis with lignite in pellet form. The use of these fuels in pellet form may increase the interaction between them during the process. In addition, the use of fuels in pellet form is important in terms of the changes in pellets during pyrolysis. It is, therefore, the objective of this work to study the pyrolysis of Soma lignite and Oil Plant Cake (OPC) to understand not only the individual pyrolysis behavior of these materials and also their blends with varied compositions. Pyrolysis experiments were carried out in a special fixed-bed vertical chamber enabling fast discharging and cooling of thermally evolved molecules during pyrolysis. Expected properties and yields of blends calculated from their individual values were taken as the main criteria in the interpretation of the results for the presence of any synergy between two materials.

EXPERIMENTAL SECTION

Materials and pellet preparation

Oil plant cake (OPC) was supplied as air-dried samples from a local oil Plant in Elazig, Turkey, and dried in an oven at 50°C until the proper moisture content (< 10%) was obtained. It was ground with a Retch automatic mortar and sieved to get a 100-200 mesh sample particle size. Soma lignite (SL), supplied by Turkish Coal Enterprises (TKI), was crushed and ground using the same mortar. After sieving, 100-200 mesh size samples were taken and dried at 105°C in the oven under nitrogen. These raw samples were maintained in closed plastic bags until use and blended to get desired mass proportion of OPC with SL. Pellets of approximately 13.0x6.0 mm diameter x height and 1.00 g mass were prepared from the blended powder by compaction under a hydraulic press. In order to avoid any error that may result from dissimilar pellet dimensions, the same amount of blends was used under a hydraulic press and the same compaction (10^4 kgf/cm^2) pressure was applied. Proximate compositions of the sample powders were determined according to ASTM-D3174 and ASTM-D3175 standard procedures. Considering that proximate analysis results somehow reflect the behavior of materials under severe thermal decomposition conditions, the same procedures were also applied to the blend pellets to elucidate any deviations from the expected levels that can be found in the following Eq.(1)

$$X_E = \frac{p}{100}\left(X_{opc}\right) + \frac{100-p}{100}\left(X_{SL}\right) \qquad (1)$$

Here, p represents percent OPC in the blend while subscripted terms denote any proximate characteristic of OPC and SL, and X_E is the expected value of that characteristic for the related blend. If X is assumed to denote the corresponding solid or liquid yield in the pyrolysis of individual materials, the same equation can be used to calculate expected yields for a particular blend. Dimensions of the pellets were also measured to determine any changes in their size during pyrolysis. Elemental compositions of OPC, SL, blends, and pyrolysis chars were determined with LECO 932 CHNS analyzer.

Equipment and procedure

Pyrolysis experiments were performed using the system shown in Fig. 1. It consists of an electrically heated vertical chamber and a quartz tube (24 mm diameter and 300 mm length) having a stainless steel wire mesh basket placed midway. Quartz tube has proper refractory caps at the top and at the bottom. The bottom cup is connected to the cooling system incorporating two U tubes and ice baths for trapping condensable products.

Before starting the runs, a quartz tube and two U tubes were dried in an oven at 105°C for 2 hours. They were pre-weighted and set on the chamber as shown in Fig. 1. After heating the chamber to pyrolysis temperature and then starting nitrogen flow at 100 ml/min, the top cap was lifted and the pre-weighted pellet was dropped on the wire mesh basket, and the cap was quickly set its place. Although, very long times are required to reach a mass equilibrium during pyrolysis at a particular temperature, which is important for accounting for all the condensable and non-condensable pyrolysis products, a duration of 20 min. was allowed for this stage because the decomposition of pellets proceeded very fast under these conditions. This time was seen to be more than enough for sweeping the pellet and collecting all the condensable products on the interior surface of the bottom section of the quartz tube and in the cooling traps. After that, the heating was stopped and the system was left to cool under the nitrogen flow. The top cap of the quartz tube was removed and the pyrolysis residue on the basket was taken and weighed. Quartz and U tubes were weighted to determine the liquid product yields and cleaned by rinsing with tetrahydrofuran. Gas yields were estimated from the difference.

Experiments were planned under three groups. In the first, OPC and SL were pyrolyzed individually to find the
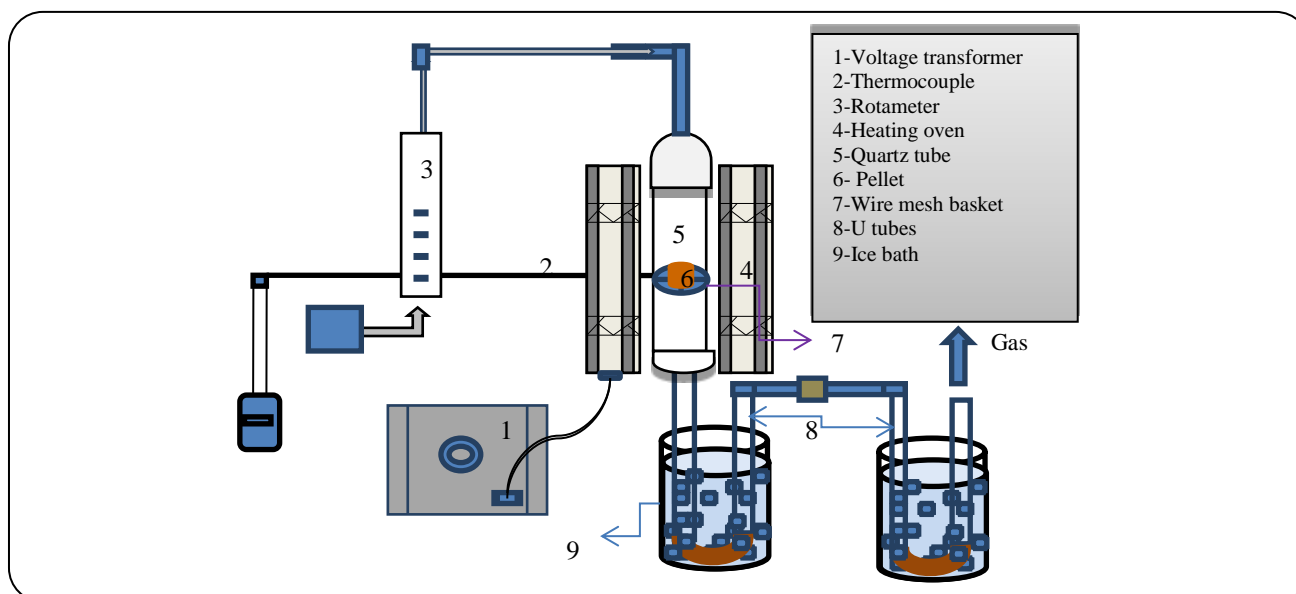
1-Voltage transformer
2-Thermocouple
3-Rotameter
4-Heating oven
5-Quartz tube
6- Pellet
7-Wire mesh basket
8-U tubes
9-Ice bath

Fig 1: Pyrolysis system.

most suitable temperature among 500, 600, and 700ºC favoring liquid yields. The second group of experiments was done with the blends at this temperature and aimed to elucidate blend composition favoring synergy between two materials. Pyrolysis yields were calculated in terms of the mass percentage of the raw materials or the blends. The third group of experiments involved runs carried out to find the effect of reaction temperature on the synergy.

RESULTS AND DISCUSSION
Properties of OPC and lignite

Proximate and elemental compositions of OPC and SL are shown in Table 1. Table 2 depicts proximate compositions of the blends with varied OPC content. The values in brackets are expected values calculated by the above equation. It is seen that the deviations from the expected values in the moisture contents can be easily regarded as laying in the experimental error limits. So, it can be taken as a bias for the accuracy of volatile matter and ash determinations. Volatile matter contents are noticeably lower and ash contents are considerably higher than the expected values. Except for the blend with 75% OPC content, fixed carbon contents show parallel changes to these as expected. This implies some kind of interaction during volatile matter and ash tests for blends with 25 and 50% OPC contents. During the co-combustion of biomass and coal, some minerals in biomass samples form ash

containing alkaline and alkaline earth oxides which can interact with alumina-silicates in coal or other blend components and slag is formed [26]. Two possible sources for these differences may be the interactions related to volatile organic matter and minerals in the two materials. Then, some of the volatile minerals in OPC may have been combined with minerals in SL during the thermal decomposition process of the standard proximate procedure. The interactions between volatile organic matter can contribute to increasing fixed carbon contents. However, volatiles evolving from the two materials may not have contacted properly when their outflow rates are high. This seems to be true in the case of a blend with 75% OPC content because evolution rates of volatiles from OPC are expected to be much higher than those of lignite. Although the differences between the elemental composition of OPC and lignite are marked; there is no need to determine the elemental composition of their blends because elemental analysis itself can't influence the amounts of individual elements.
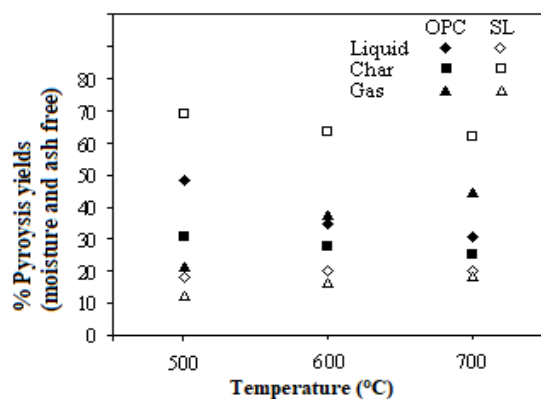
Pyrolysis of individual OPC and SL

The changes in the pyrolysis yields of OPC and SL with the temperature are given in Fig. 2. OPC gives much more liquid and gas yields compared to SL and thus, less char has remained after its pyrolysis under the same conditions. As discussed above, this is due to the differences in the molecular structure of the two materials. The chemical structure of coals usually contain

Table 1: Proximate and elemental analysis results

Samples	SL	OPC
Proximate analysis (weight %)		
Moisture	6.7	4.8
Ash	5.7	4.9
Volatile matter	53.4	77.7
Fixed carbon	34.2	12.6
Elemental analysis (moisture and ash-free basis, weight%)		
C	65.8	46.1
H	4.5	6.8
N	0.8	1.5
S	1.1	-
O (by difference)	27.8	45.6

Table 2: Proximate analysis results of the blends.

OPC content (%)	25	50	75
Moisture	6.5 (6.3)	5.6 (5.8)	5.7 (5.4)
Ash	6.9 (5.5)	6.0 (5.3)	7.3 (5.1)
Volatile matter	59.7 (65.8)	62.8 (71.4)	74.5 (77.0)
Fixed carbon	26.9 (22.4)	25.6 (17.5)	12.5 (12.5)

Fig.2: Individual pyrolysis yields of OPC and SL.

poly-condensed aromatic hydrocarbon bonds (-C=C-) which are stronger than ether bonds (R-O-R) of cellulose, hemicelluloses, and lignin composing the structure of biomasses [27]. Both liquid and solid yields of OPC decrease considerably with temperature. Although SL exhibits similar behavior, its changing level seems much less compared to OPC. Thus, the most suitable temperature

favoring liquid yields is 500ºC for OPC. In a similar study [28], the same result is reported. Apparently, the most suitable temperature for SL favoring high liquid and low gas yields is 600ºC. It may be envisaged that SL is more effective than OPC in the behavior of the blends. So, it seems reasonable to prefer 600ºC to search for the effect of blend composition on the pyrolysis yields when the interaction between OPC and SL during the proximate analysis of the blends, with 25 and 50% OPC contents are considered.

The changes in the pyrolysis yields of OPC-SL blends with increasing OPC content are given in Fig. 3, on which corresponding values for expected yields are also depicted. It is clear that 0 and 100 % OPC contents on the abscissa correspond to individual SL and OPC respectively. For the blends with 25 and 50% OPC contents, observed liquid yields are noticeably lower and char yields are higher than expected levels. This implies some synergy between two materials for these compositions in terms of solid yields and might have resulted from the interactions between the chemical structures evolving upon fast decomposition of OPC and SL to form larger molecules which give rise
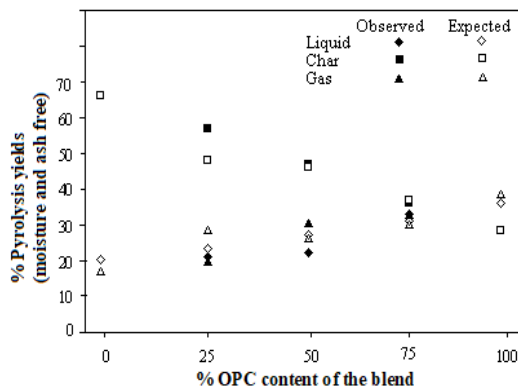
Fig.3: Pyrolysis yields of OPC-SL blends at 600ºC.

Fig.4: Pyrolysis yields of blends containing 75%OPC.

to the amount of char and gas. It is quite probable that outflow rates of volatiles from the decomposing blend pellet may be high compared to pellets composed from SL alone because the decomposition rate of biomasses is generally higher than coals. This explains why the differences between observed and expected values diminish with increasing OPC ratio. This is confirmed by the yields of the blend with 75% OPC content. Here OPC and SL seem to behave individually and the interactions between the evolving chemical structures are not severe enough to be effective on the yields due to very high outflow rates of volatiles from the decomposing blend. For this reason, this composition was chosen to search for the effect of temperature on the level of interaction.

For the blend containing 75% OPC, changes in the yields with increasing pyrolysis temperature are given in Fig. 4 with corresponding values for expected yields. All the values, except expected gas yield, intercept at 500ºC. This is an interesting behavior considering individual yields given in Fig. 2. It can be pointed out that 75% OPC is a fitting composition resulting in yields close to each other at 500ºC without any mutual interaction. At 700ºC, the observed liquid yield is slightly lower, and the char yield is higher than the expected levels. This implies some synergy between the two materials for this temperature in terms of solid yield, which is absent for the other two temperatures. Here, it is seen that both the composition of the lignite-biomass blend and pyrolysis temperature determines the extent of interaction between the two materials. Thus, the deviations from expected values at 700ºC might have resulted from increased severity of interactions between the chemical structures
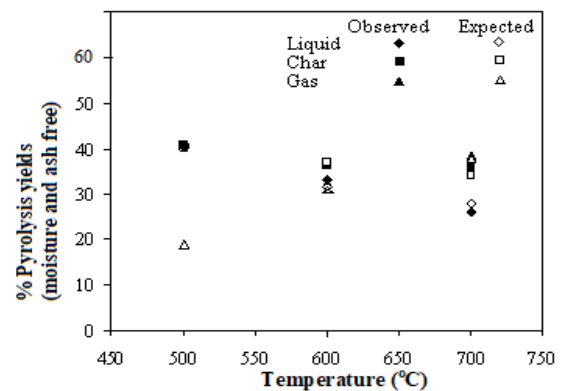
evolving upon fast decomposition of OPC and SL. These conditions support the formation of char and gas.

Liquid yields are generally the most preferred product in pyrolysis. For this reason, special importance has been given to the conditions that would maximize liquids. The experimental data given in Figs. 2-4 are combined and set to undertake a two-factor-multi level linear regression to search for a model for the liquid yields. Fig. 5 is a contour plot derived from this analysis and shows changes in liquid yields from blends as iso-yield regions with pyrolysis temperature and SL% of the blend. Changing the direction of iso-lines imply that SL% of the blends and pyrolysis temperature inversely affect liquid yields. In this graph, the maximum liquid yield region corresponds to compositions greater than 75% OPC (25% SL) as is pointed out above. With coded values between 1 and -1 for maximum and minimum temperatures and SL% factors, the regression equation given below shows the relation between liquid yields and coded values of pyrolysis temperature (CT) and lignite content of the blends (CSL%), with an interaction term for these factors. changes in liquid yields

$$Liquid\,(\%) = 29.136 - 5.644CT - 3.295CSL\% + 1.933CT.CSL\%$$

Proximate analyses of the chars left after pyrolysis and their expected values found by using individual values and blend composition are given in Table 3. Both volatile matter and ash contents of the blend chars are noticeably lower than the expected values. As a consequence, their fixed carbons are higher than expected levels. These are contradictory to the results of pyrolysis char yields which are slightly higher than expected levels as shown above.

Table 3: Proximate analysis of pyrolysis chars.

Temperature (ºC)	Chars from	Volatile matter,%	Ash,%	Fixed Carbon*,%
500	SL	28.7	8.6	62.7
	OPC	31.0	22.7	46.3
	75%OPC Blend	28.7 (30.4)	17.1(19.2)	54.2 (50.4)
600	SL	22.9	9.3	67.8
	OPC	26.3	22.9	50.8
	25%OPC Blend	22.3 (23.8)	11.4 (12.7)	66.3 (63.5)
	50%OPC Blend	19.3 (24.7)	14.7(16.0)	66 (59.3)
	75%OPC Blend	19.5 (25.5)	18.8(19.5)	61.7 (55)
700	SL	15.9	10.2	73.9
	OPC	25.1	24.4	50.5
	75%OPC Blend	20.2 (22.8)	19.9(20.9)	59.9 (56.3)

*:by difference.
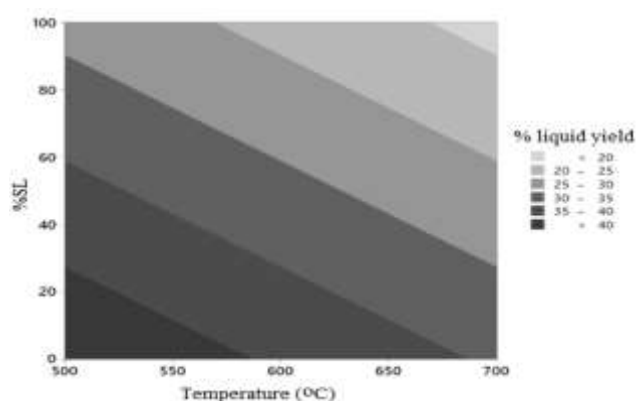
Fig. 5: Contour plot of liquid yields.

A reasonable explanation implies that more volatile matter than expected levels should have evolved from these chars in the volatile matter test and interactions between volatiles evolving from blend chars during this test result in increased amounts of chars.

Ash contents of the blend chars seem slightly lower than expected levels. This is contradictory again with raw blends of OPC and SL which give higher-than-expected amounts of ash. This may be explained by the volatile minerals in OPC, which combine with minerals in SL during the standard proximate procedure, giving rise to ash contents. These minerals should have been volatilized without

any reaction during pyrolysis over which the temperatures are very much lower than those in the proximate procedure.

The dimensional changes in the pellets of OPC, SL, and their blends after fast pyrolysis are given in Table 4. Here, D_p/D_0 and h_p/h_0 represent respectively ratios of residue pellet diameter and length to their initial values. As is seen in Table 4, all kinds of pellets undergo contraction more or less, with major contractions in the radial direction. These are especially evident for 600 and 700ºC temperatures because axial changes are not considered at these temperatures. This implies extensive changes during pyrolysis, which cannot be explained by thermal decomposition only. It is interesting that the differences between the two-dimensional changes are not considerable at 500ºC. It can be explained by lower outflow rates of volatiles from both lateral and top surfaces of the pellet compared to those occurring at 600 and 700ºC temperatures. Outflow rates from the top surface may increase greatly at these temperatures because of the larger outflow surface and shorter flow path compared to the radial direction. These fast evolution and outflow of volatiles may force the pellet to swell and increase axial length.

CONCLUSIONS

From the discussions above, the following conclusions can be drawn:

Table 4: The changes in the dimensions of pellets after pyrolysis.

Temperature (ºC)	Samples	D_p/D_0(%)	h_p/h_0(%)
	SL	92.3	93.8
500	OPC	79.5	84.8
	75%OPC Blend	84.0	89.7
	SL	91.9	100
	OPC	84.6	96.8
600	25%OPC Blend	90.1	100
	50%OPC Blend	87.5	95.6
	75%OPC Blend	85.6	98.5
	SL	88.5	98.4
700	OPC	83.8	100
	75%OPC Blend	85.4	104.6

i. Proximate analysis results of the blends of lignite and oil plant cake may be different from expected values.

ii. The yield of liquid product obtained from the pyrolysis of raw lignite is always much lower than oil plant cake at operating temperatures, due to the different decomposition temperatures.

iii. The liquid product yield of raw oil plant cake did not show a regular change with temperature due to secondary decomposition reactions.

iv. For blends with compositions lower than 50% oil plant cake, the interactions between the chemical structures evolving upon fast decomposition of oil plant cake and lignite can form a synergy that gives rise to the amount of char and gas.

v. Both the composition of the lignite-oil plant cake blend and temperature determine the extent of interaction between these materials during pyrolysis.

vi. Proximate analysis parameters of the chars obtained from blends of lignite and oil plant cake may be different from expected levels due to synergy during thermal decomposition in the proximate test.

vii. Blend pellets undergo extensive changes during pyrolysis with major contractions in the radial direction. Fast evolution and outflow of volatiles force the pellets to swell and increase axial lengths.

viii. Further research is needed to explore the chemical properties of liquid and gas products of pyrolysis, and the reactivity and surface characteristics of chars.

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