

## Synergetic effect of biomass mixture on pyrolysis kinetics and biocrude-oil characteristics

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(Received 8 June 2015 • accepted 31 August 2015)

**Abstract**—Biocrude-oil characteristics were investigated from fast pyrolysis of a mixture of Douglas fir and coffee ground. The mixture was prepared on a 1 : 1 weight basis and pyrolyzed in a bubbling fluidized bed reactor. Characteristics of biocrude-oil were compared at various reaction temperatures ranging from 673-873 K. The mixture resulted in a more improved quality biocrude-oil than each biomass feedstock at the reaction temperature of 823 K with significantly low atomic ratio of 0.43 O/C. The kinetic parameters for biomass decomposition were investigated through Friedman, KAS, FWO and CC isoconversional models. In mixture pyrolytic conversion range of 0.1-0.8, the average activation energy was found to be 135 kJ/mol. The results showed that pyrolysis of coffee ground with Douglas fir has more synergetic effect than individual biomass, which leads to a potentially higher quality fuel with lower activation energy to that of biomass.

Keywords: Biocrude-oil, Fast Pyrolysis, Biomass Mixture, Kinetic Models, Atomic Ratio

### INTRODUCTION

Since the first IPCC report in 1990, when the world officially agreed to the long standing debate of anthropogenic global warming, along with the near global ratification of Kyoto Protocol in 1997, fossil fuel based CO<sub>2</sub> emissions are still on the rise and are expected to peak in the near future. Renewable energy is considered to be a solution that could not only reduce CO<sub>2</sub> emissions but also sustain increase of energy consumption. Biomass is a practical source of renewable energy in the world as much as 14% of world's energy consumption [1], which has advantages in carbon neutral and low sulfur content. Waste biomass resources are currently an attractive renewable energy option as much as a waste disposal remedy. For instance, 500-600 billion cups of coffee is consumed globally, and Asian coffee market projects a consumption of 1740 million kg by the year 2020 [2], thus sustainably leaving behind a large stock of bioenergy potent coffee ground, rich in organic compounds with no significant market.

Biomass waste can produce absorbents, fuels and chemical feedstock through pyrolysis. Biocrude-oil is a secondary liquid fuel produced through fast pyrolysis, and is generally acidic, contains high level of oxygen (35-40%), high water content (15-35%), thus lowering the heating value (17 MJ/kg) as opposed to petroleum fuels (40 MJ/kg), alongside fuel instability [3]. Table 1 elaborates the previous studies on biocrude-oil characteristics of various biomasses [4-9]. In terms of higher heating value (HHV), the biocrude-oil

quality is better when the oxygen content denoted by the O/C atomic ratio is smaller while the H/C ratio is larger, thus acting as an indicator in differentiating quality of biocrude oil. The O/C ratio in petroleum products is known generally to be less than 0.06, while the H/C ratio ranges from 1.5-2.0 [10]. To overcome the high comparative O/C atomic ratio disadvantages, there have been studies on the biocrude-oil production from the mixture of biomass and low oxygen compounds such as almond shell and high density polyethylene [11], biomass and waste tire [12]. But the systematic study on the biocrude-oil from the mixture of different kinds of biomass is rather sparse. Mixing of biomass could affect the pyrolysis behavior, and the characteristics of produced biocrude-oil might be enhanced in comparison with those from individual biomass feedstock.

Thermogravimetric slow pyrolysis enables investigation of thermal degradation properties and curves and devolatilization of hemicellulose, cellulose and lignin can be understood systematically. Thus, it was envisaged to carry out slow pyrolysis for the mixture. Kinetic analysis of the mixture was performed to understand the pyrolysis characteristics of the mixture and to envisage reaction mechanism during pyrolysis of mixture.

This study focuses on slow pyrolysis investigation of thermal degradation and devolatilization process for a biomass mixture of Douglas fir and coffee grounds, through TGA and kinetic analysis. The product coffee-fir biocrude-oil from fast pyrolysis was subject to elemental analysis to determine the quality. The new results are compared with previous pyrolysis studies on individual biomass of Douglas fir [6,7] and coffee grounds [9,13]. The study is to further establish the synergetic effect of biomass mixing on producing superior quality coffee-fir biocrude-oil.

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**Table 1. Synopsis bio-oil characteristics of ultimate analysis, atomic ratios and HHV of existing studies**

Bio-oils	Ultimate analysis (wt%)					Atomic ratio		HHV (MJ/kg)
	C	H	N	S	O	O/C	H/C	
Rice husk [4]	39.9	8.1	0.6	0.0	51.4	0.96	2.45	16.5
Wheat straw [5]	52.3	9.4	1.9	0.6	35.8	0.51	2.16	25.4
Pinewood [5]	54.4	9.6	1.6	0.4	34.0	0.47	2.12	26.6
Douglas fir[6,7]	44.1	7.4	0.5	0.0	47.9	0.81	2.01	18.4
Palm EFB [8]	40.9	10.7	1.2	0.0	47.2	0.86	3.14	23.7
Timothy grass [5]	49.2	9.3	2.2	0.9	38.4	0.58	2.27	23.8
Coffee ground [9]	54.3	7.4	3.1	0.0	35.3	0.49	1.64	20.4
Palm shell [8]	38.1	9.1	0.6	0.0	52.2	1.02	2.87	20.0
Mallee [9]	42.3	8.2	0.1	0.0	49.4	0.88	2.33	17.9

**Table 2. Proximate and Elemental analysis of Douglas fir, coffee ground and mixture of the two**

	Individual biomass		Douglas fir and coffee ground 1 : 1 mixture this study
	Douglas fir	Coffee ground	
Proximate analysis (wt%)			
Water content	3.7	0.9	2.4
Volatile	77.7	78.3	78.0
Fixed carbon	16.6	16.0	16.3
Ash	2.0	4.8	3.4
Elemental analysis (wt%) <sup>a</sup>			
C	49.1	53.7	50.6
H	6.1	7.1	6.4
O <sup>b</sup>	44.8	36.8	42.3
N	0.0	2.4	0.7
S	0.0	0.0	0.0
HHV (MJ/kg)	18.4	22.7	20.7
Bulk density (kg/m <sup>3</sup> )	256	414	341
H/C atomic ratio	1.49	1.59	1.52
O/C atomic ratio	0.68	0.51	0.63

<sup>a</sup>Dry, ash-free basis

<sup>b</sup>By difference

## MATERIALS AND METHOD

### 1. Sample Preparation and Biomass Characteristics

The Douglas fir and coffee ground were dried in a dry oven at 105 °C for 24 hours, which reduced the moisture content to 6-9 wt%. Since both feedstocks can absorb moisture with time, moisture of Douglas fir can increase to 9-11 wt% and coffee grounds to 10-13 wt% due to its high porosity. Therefore, before each experiment, the Douglas fir and coffee ground were subjected to a second stage of drying for 18 hrs of dry oven at 110 °C to ensure feed moisture content was 1-3 wt% for both feedstock, and they were mixed on a 1 : 1 (wt basis) just before the experiment. The moisture content was measured based on ASTM D5142 moisture analysis using LECO TGA701 thermogravimetric analyzer. Sizing of Douglas fir and coffee ground was carried out using testing sieves to size the particles within 0.85-2 mm.

The physicochemical properties of Douglas fir, coffee ground

and the mixture used in the present experiment are illustrated in Table 2. Proximate Analysis involved using an LECO TGA701 thermogravimetric analyzer with the precision of  $\pm 0.02\%$  RSD (relative standard deviation). The elemental analysis was carried out by Flash EA 1112 series, and the analysis for the mixture gave results of H/C atomic ratio of 1.52 and O/C atomic ratio of 0.63. Douglas fir atomic ratios of H/C and O/C are 1.49 and 0.68, respectively. Coffee ground atomic ratios of H/C and O/C are 1.59 and 0.51, respectively. A bomb calorimeter (LECO AC-500) with accuracy of 0.11% was used to measure the higher heating value (HHV) following ASTM D2015 with an average of three samples each time of feedstock and biocrude-oil. HHV of Douglas fir, coffee ground and the 1 : 1 mixture were 18.4, 22.7 and 20.7 MJ/kg, respectively. Notably, coffee ground contains more nitrogen than Douglas fir due to high proteins and caffeine [14].

### 2. Experiment

The experiments for the fast pyrolysis of the mixture were con-

ducted in a bubbling fluidized bed reactor. Detailed illustration of equipment and operations is provided in previous studies [15,16]. Previous studies show that the optimum yield of biocrude-oil from sawdust is obtained at 773 K [4,5,16] and coffee ground at 823 K [9]. The experiments were carried out for one hour and 200 g of mixture were subjected to investigation for each reaction temperature.

## THEORY

### 1. Thermogravimetric Analysis

The tests for TGA were under inert nitrogen atmosphere using LECO TGA701 thermogravimetric analyzer. The degree of conversion of the mixture ( $\alpha$ ) is defined by Eq. (1)

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_f)} \quad (1)$$

where  $W_0$ ,  $W_f$  and  $W_t$  are the initial sample mass, final sample mass, the sample mass at specific time  $t$  respectively. The heating rates ( $\beta$ ) were designed to be slow pyrolysis, controlled at  $\beta=5, 10, 15$  and  $20$  K/min. For each heating rate, three crucibles of 2-3 g pre-mixed sample of 1:1 wt basis with particle size similar to that of experimental pyrolytic conditions were placed on the thermo balance.

### 2. Kinetic Models

In this study, four isoconversional models were investigated to compare the activation energy: differential Friedman, integral Flynn-Wall-Ozawa (FWO), integral Kissinger-Akahira-Sunose (KAS) and differential Chatterjee-Conrad (CC). For conversion values from 0.1-0.8, Friedman differential method presented the best  $R^2$  values represented in Table 3. Integral models present weaknesses such as needing Picard iteration of the temperature integral, integral methods are prone to error accretion during such successive approximations and the temperature integral requires boundary conditions which are frequently ill defined [17]. Thus, Friedman differential model results were used for an understanding of the lignocellulosic mixture decomposition kinetics similar to that of other studies [18-22].

The Friedman differential isoconversional technique is denoted by Eq. (2) [18]

$$\ln\left[\frac{d\alpha}{dt}\right] = \ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = \ln[Af(\alpha)] - \left[\frac{E_a}{RT}\right] \quad (2)$$

where  $\beta$  is the constant heating rate,  $d\alpha/dt$  is the rate of conversion,  $d\alpha/dT$  is the non isothermal reaction rate,  $A$  is the frequency or pre-exponential factor ( $s^{-1}$ ),  $f(\alpha)$  is the function expressing the dependence of the reaction rate on the conversion,  $E_a$  is the apparent activation energy (kJ/mol),  $R$  is the universal gas constant (8.3144 J/mol-K),  $T$  is the temperature (K).

The activation energy  $E_a$  of the mixture can be determined through the Friedman integral kinetic model described in Eq. (2). For a specified degree of conversion ( $\alpha$ ), the dataset ( $x, y$ ) can be determined at each heating rate ( $\beta=5, 10, 15, 20$  K/min) where  $x$  is  $1/T$  and  $y$  is the left-hand side in the kinetic model to be applied. At a specified value of  $\alpha$ , linear curve fitting is performed on the datasets from various heating rates, which becomes the isoconversional lines. The activation energy  $E_a$  can be determined through the slope of the isoconversional line at each value of  $\alpha$ .

Pre-exponential factor ( $A$ ) can be obtained from the intercept of the isoconversional line. If we take  $f(\alpha)=\alpha^n$  in the Friedman model in Eq. (2) where  $n$  is the reaction order, the intercept can be expressed as follows:

$$\ln[A\alpha^n] = \ln(A) + n\ln(\alpha) \quad (3)$$

At a specified reaction order, the pre-exponential factor ( $A$ ) can be determined for each degree of conversion ( $\alpha$ ).

## RESULTS AND DISCUSSION

### 1. Thermogravimetric Analysis

Fig. 1 shows thermogravimetry (TG) and differential thermogravimetry (DTG) curves as a function of temperature, by which investigation of mixture thermal degradation was concluded. TG and DTG curves show three distinct stages in compliance with that of other organic pyrolysis, for increasing temperature, which can be categorized as vaporization and surface volatile removal stage, active pyrolysis stage and passive pyrolysis stage.

The small change of conversion initially found is attributed to the first stage of decomposition, which is the vaporization of mois-

**Table 3. Results of activation energy as a function of conversion for Friedman, FWO, KAS and CC models**

Conversion ( $\alpha$ )	Friedman differential model		Chatterjee conrad differential model		FWO integral model		KAS integral model	
	$E_a$ (kJ/mol)	$R^2$	$E_a$ (kJ/mol)	$R^2$	$E_a$ (kJ/mol)	$R^2$	$E_a$ (kJ/mol)	$R^2$
0.1	87.7	0.997	79.0	0.950	74.3	0.939	89.6	0.998
0.2	70.3	0.983	91.5	0.983	86.9	0.979	72.9	0.984
0.3	85.0	0.968	92.2	0.986	87.4	0.983	92.1	0.967
0.4	120.5	0.956	101.3	0.976	96.7	0.971	123.9	0.956
0.5	155.2	0.952	117.9	0.963	113.8	0.956	161.4	0.952
0.6	160.8	0.981	136.3	0.972	132.9	0.967	166.8	0.979
0.7	151.0	0.972	139.2	0.982	135.8	0.979	158.0	0.969
0.8	255.0	0.847	132.0	0.835	127.6	0.811	263.7	0.849
0.9	1052.1	0.905	625.9	0.993	646.0	0.993	1100.6	0.909
Average 0.1-0.8	135.7	0.9570	111.2	0.9559	106.9	0.9481	141.5	0.9567

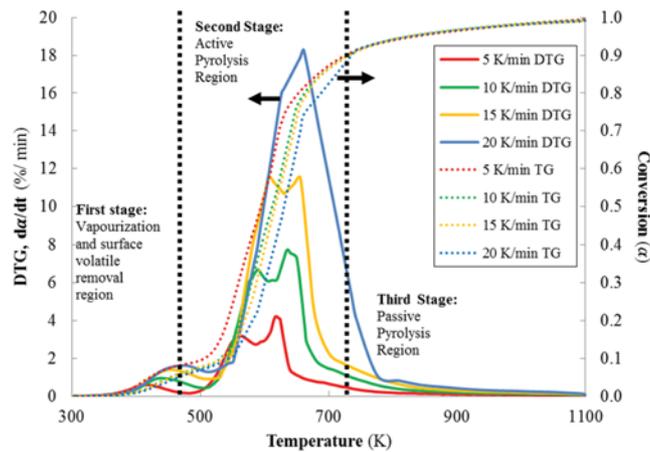


Fig. 1. Effect of pyrolysis rate (TG and DTG curves) of Douglas fir and coffee ground 1 : 1 wt% mixture.

ture and volatile components adhering to the surface of the samples that occurs from room temperature to about 473 K. The second stage of active pyrolysis, demonstrated by the steepest slopes of the curves, has the largest sample weight loss that occurs from 473–723 K and two DTG peaks were observed. The first peak is attributed to mainly hemicellulose decomposition peak at lower temperatures (473–673 K), and the second peak is attributed to mainly cellulose decomposition (573–723 K). The decomposition of lignin, which generally has a broad decomposition temperature range, occurs from 473–773 K and spans into the passive pyrolysis stage, where it decomposes slowly alongside char as per Fig. 1. They generally overlap each other. In the lower heating rates, distinct two DTG peaks can be found while the peaks merge as the heating rates are increased. Passive pyrolysis follows at about 723 K, which completes hemicellulose, cellulose and lignin decompositions that constitute the third stage of pyrolysis. Based on this result, the lower limit of the pyrolysis reaction temperatures was set at 673 K, as 723 K completes 90% of conversion, irrespective of increasing heating rates, observed in four slow pyrolysis heating rates. Thus, the range of the reaction temperature was carefully projected for fast pyrolysis to be at 673 (60–80% conversion), 723 (80–90% conversion), 773 (90–95% conversion), 823 (95–97% conversion) and 873 K (97–98% conversion), to determine the effects of pyrolysis temperature on coffee-fir biocrude-oil quality.

The effect of heating rates can be observed from Fig. 1. The lower heating rate denoted better conversion while higher heating rates had lower conversions below 773 K as shown in the TG curve. This could be due to heat and mass transfer limitations of particles, which can result in a heat transfer temperature gradient within the particle, prompting more heat supplied, which is represented by the increase in temperature, for it to reach the same conversion level of the samples heated at lower heating rates, as shown by another study [21]. The graphs indicate no effect in heating rates at conversion level greater than 773 K. Thus slow pyrolysis enables in understanding the decomposition process and can be used to project fast pyrolysis phenomenon. This result also suggests that the importance of feedstock preparation of small, homogeneous particles with large heat transfer surface for efficient pyrolysis.

## 2. Kinetic Analysis

As denoted by Fig. 1 the change in conversion is predominant between 473–723 K, corresponding to the main active pyrolysis stage where hemicellulose, cellulose and lignin decomposition occurs, overlapping each other. Activation Energy  $E_a$  is the minimum energy required for a reaction to commence and higher the value, slower the reactions will take place. The kinetic results show that activation energy depends on conversion, which means reaction characteristics are varied in the pyrolysis process. Activation Energy is derived from isoconversional lines through various methods and Friedman differential isoconversional method is presented in Fig. 2. Similarly, activation energy was derived for FWO, KAS and CC models from respective isoconversional lines summarized in Fig. 3.

Fig. 4 shows the change in activation energy with progressing conversion values for the feed mixture. Different reaction mechanisms are responsible for change in  $E_a$  values as conversion increases. Because activation energy is the minimum amount of energy required for a reaction to begin, the higher the  $E_a$  values, slower reac-

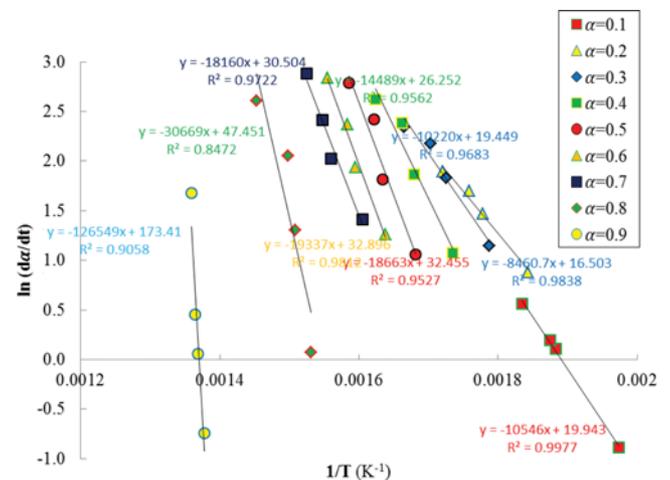


Fig. 2. Friedman differential isoconversional curves for the calculation of activation energies of Douglas fir and coffee ground 1 : 1 wt% mixture.

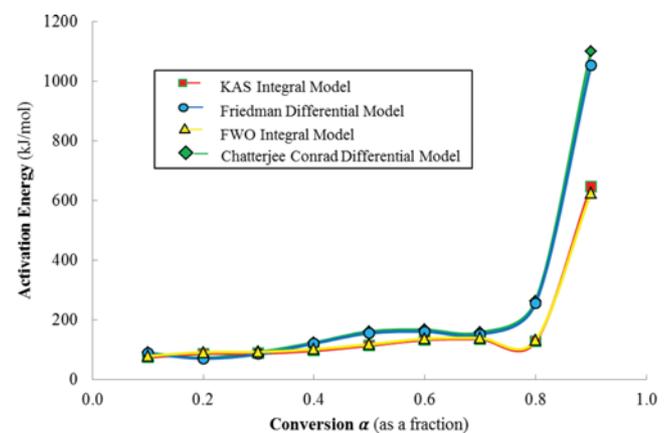


Fig. 3. Calculated activation energy by KAS and FWO integral models and Friedman and Chatterjee-Conrad differential models for heating rates of 5, 10, 15 and 20 K/min for pyrolysis of Douglas fir and coffee ground mixture on a 1 : 1 wt% ratio.

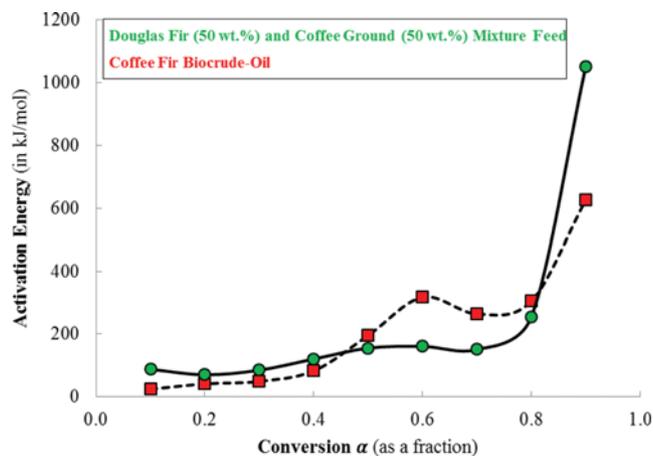


Fig. 4. Calculated activation energy Friedman differential models for heating rates of 5, 10, 15 and 20 K/min for slow pyrolysis of Douglas fir and coffee ground mixture on a 1 : 1 wt% ratio denoted in solid line and pyrolysis of Coffee-fir Biocrude-oil denoted in dashed line.

tions will proceed. The sudden increase of  $E_a$  in conversion values of over 0.8 is known to be due to devolatilization of char after main reaction [20-22]. Most of the hemicellulose and cellulose were decomposed at pyrolytic conversion of 0.1-0.8. It was found that activation energy increases drastically in conversion values of over 0.8. Thus conversion value 0.9 was omitted in this study so as to focus more on the contribution of main organic reactions in estimating the average activation energy of mixture.

With respect to Friedman method, the average activation energy is 135.7 kJ/mol for the conversion values of 0.1-0.8. This value is between the activation energies of individual feedstock, where the average  $E_a$  of Coffee Ground and Douglas fir was calculated to be 120.2 kJ/mol and 155.3 kJ/mol, respectively, and is represented in Fig. 5, which also establishes the synergetic effect of the mixture through kinetic analysis, as the mixture maintains a low activation energy overall within conversion values of 0.1-0.8, to that of coffee ground and Douglas fir.

The activation energy of the mixture (135.7 kJ/mol) was lower than that for wood pyrolysis (155.3 kJ/mol) as well as reported values previously. Note that the study on oak tree residues shows the

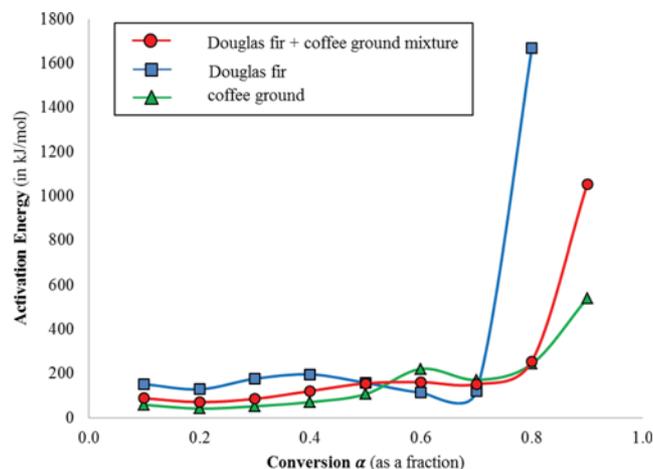


Fig. 5. Mixture activation energy comparison with individual pyrolysis of Douglas fir and coffee ground.

average activation energy of 236 kJ/mol [20], and forest wood study presents the activation energy range of 122-233 kJ/mol [23]. In forest wood study, the activation energy was 81-287 kJ/mol [24].

The pre-exponential factors which were calculated by Eq. (3) through Friedman model are listed in Table 4, where the reaction orders were assumed as  $n=0, 1, 2$ , respectively. The pre-exponential factors were in the range  $10^7$ - $10^{20} \text{ s}^{-1}$  between conversion 0.1-0.8, while the pre-exponential factor increased drastically to  $10^{75}$  at conversions of 0.9. This is probably due to the devolatilization of residual char as discussed before. The pre-exponential factors obtained in the present study were within similar range to those of other studies ( $10^7$ - $10^{22} \text{ min}^{-1}$ ) for forest residues [24].

### 3. Characteristics of Coffee-fir Biocrude-oil

Coffee-fir biocrude-oil produced at reaction temperature of 823 K resulted in highest product yield (% of weight of collected product vs weight of total feedstock) of 54%, highest energy yield (product yield  $\times$  ratio of  $\text{HHV}_{\text{product}}$  vs  $\text{HHV}_{\text{feed}}$ ) of 55%, and highest HHV of 21.4 MJ/kg [15]. In this study the focus is on explaining the synergetic effect of the mixture in producing a superior quality biocrude-oil, through kinetic data and elemental composition.

The pyrolysis kinetics of coffee-fir biocrude-oil were investigated. Activation energies for coffee-fir biocrude-oil, Friedman differential method is presented in Fig. 4. Note that for the conversion fac-

Table 4. Calculated pre-exponential factor for the mixture through Friedman differential model

Conversion	$E_a$ (kJ/mol)	Intercept	Pre-exponential factor ( $\text{s}^{-1}$ )		
			n=0	n=1	n=2
0.1	88	19.94	4.569E+08	4.569E+09	4.569E+10
0.2	70	16.50	1.465E+07	7.325E+07	3.663E+08
0.3	85	19.44	2.771E+08	9.238E+08	3.079E+09
0.4	120	26.25	2.513E+11	6.283E+11	1.571E+12
0.5	155	32.45	1.238E+14	2.477E+14	4.954E+14
0.6	161	32.89	1.923E+14	3.205E+14	5.341E+14
0.7	151	30.50	1.762E+13	2.517E+13	3.596E+13
0.8	255	47.45	4.048E+20	5.060E+20	6.325E+20
0.9	1052	173.40	2.026E+75	2.251E+75	2.501E+75

**Table 5. Bio-oil properties of pyrolysis of fir and coffee ground 1 : 1<sub>(wt. basis)</sub> mixture at varying reaction temperatures**

Parameters	673 K	723 K	773 K	823 K	873 K
Ultimate analysis (%w/w)					
C	48.54±2.74	52.00±3.72	51.41±1.25	56.98±8.58	43.00±3.95
H	7.87±0.12	8.49±0.58	8.30±0.21	9.12±1.02	6.82±1.18
N	1.34±0.04	1.29±0.13	1.33±0.09	1.33±0.29	1.28±0.51
S	0.00	0.00	0.00	0.00	0.00
O <sup>a</sup>	42.25±2.90	38.22±4.43	38.96±1.55	32.57±9.89	51.10±5.64
H/C molar ratio	1.94	1.96	1.94	1.92	1.90
O/C molar ratio	0.65	0.55	0.57	0.43	0.89
HHV (MJ/kg)	18.29	20.03	20.46	21.39	17.84
Moisture (% wt base)	21.56	21.63	22.99	21.38	28.02
Product yield [15]	27%	41%	49%	54%	51%
Energy yield [15]	24%	40%	48%	55%	43%

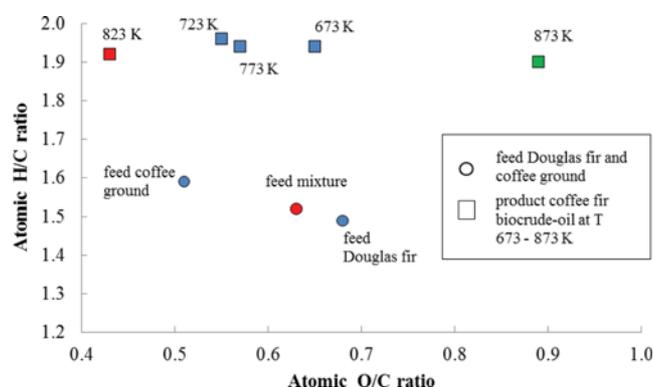
<sup>a</sup>By difference

tors of 0.1-0.5, lower activation energy was required with respect to solid feed biomass of coffee ground and Douglas fir denoted in Fig. 5, establishing the value of biocrude-oil as a liquid secondary energy source.

#### 4. Elemental Composition

##### 4-1. Optimum Reaction Temperature Dependency

The results of the elemental analysis for biocrude-oil are summarized in Table 5 throughout the reaction temperature range, and the quality of biocrude-oil is defined by atomic ratios of H/C and O/C, which are also shown. As denoted by the van Krevelen diagram in Fig. 6, a reaction temperature of 823 K gives the optimum H/C and O/C atomic ratios with values of 1.92 and 0.43, respectively. The H/C atomic ratios ranging from 1.90-1.96 were fairly stable (3% variance) for all reaction temperatures under investigation. O/C atomic ratios vary significantly (over 100% variance) and this study found that the optimum reaction temperature at 823 K results in lowest O/C ratio of 0.43, which indicates the enhanced biocrude-oil quality. In comparison, the atomic ratios of feed coffee-fir mixture have H/C and O/C atomic ratios of 1.52 and 0.63, respectively, which again supports the advantages of liquid secondary energy sources.



**Fig. 6. Van Krevelen Diagram for feed and product biocrude-oil for reaction temperature range of 673 to 873 K for the pyrolysis of Douglas fir and coffee ground on a 1 : 1 wt% ratio.**

##### 4-2. Synergetic Effect of Coffee-fir Biocrude-oil

Based on O/C ratio, it is established that a superior quality of biocrude-oil has been identified through fast pyrolysis of coffee-fir at reaction temperature of 823 K. This synergetic effect is highlighted with biocrude-oil having a similar H/C and much lower O/C than fast pyrolysis of only Douglas fir [6,7] alongside much higher H/C and lower O/C than fast pyrolysis of only coffee ground [9]. It is notable that the O/C ratio found at reaction temperature of 823 K is significantly lower than previous studies [4-9] near atmospheric pressure pyrolysis reactors. In comparison to that of solid agropellets made of spent coffee ground (1.76 H/C, 0.33 O/C) blended with pine sawdust (1.55 H/C, 0.74 O/C) [25], coffee-fir biocrude-oil is secondary liquid energy source with superior H/C and O/C atomic ratios of 1.92 and 0.43, respectively. It can be established that coffee-fir biocrude-oil has a synergetic effect of Douglas fir and coffee ground. The possible scientific explanation that could lead to the synergetic effect is based on the constituents of each biomass and its pore structure. Further studies are needed to elaborate how primary and secondary decomposition reactions are enhanced by this particular mixing. Further studies are also necessary to establish the hypothesis of pore structure formation especially with caffeine and other compounds extracted off coffee ground, and its influence in the mixture with Douglas fir.

## CONCLUSIONS

This study establishes the superior quality of coffee-fir biocrude-oil produced at reaction temperature 823 K through elemental analysis. The study elaborates the thermal decomposition through slow pyrolysis and highlights synergetic effect through kinetic analysis for the mixture with respect to individual Douglas fir and coffee ground. Superiority of Coffee-fir Biocrude-oil was further established compared to other biocrude-oil in previous studies based on its H/C ratio of 1.92 and a uniquely smaller O/C atomic ratio of 0.43 for biocrude-oil at reaction temperature of 823 K.

Kinetic analysis results showed that there is lower activation energy required with respect to woody biomass and is attributed to synergetic effect. The range and average activation energy for the

biomass waste mixture was 70-255 kJ/mol and 136 kJ/mol, respectively, for conversion values of 0.1-0.8. For the above conversion values, the pre-exponential factors were in the range  $10^7$ - $10^{20}$  s<sup>-1</sup>.

Based on this study, it can be recommended that pyrolysis of Douglas fir and coffee ground can provide a sustainable, high quality biocrude-oil.

### ACKNOWLEDGEMENT

The authors would like to thank the Korea Ministry of Science, ICT and Future Planning, and University of Science and Technology under the Ministry of Education and Human Resources for supporting this study.

### NOMENCLATURE

A	: pre-exponential factor [s <sup>-1</sup> ]
E <sub>a</sub>	: apparent activation energy [kJ/mol]
f(α)	: function expressing the dependence of reaction rate on the conversion
g(α)	: integrated reaction model
k	: reaction rate constant [s <sup>-1</sup> ]
n	: reaction order
R	: gas constant [8.314 J/mol·K]
T	: absolute temperature [K]
T <sub>m</sub>	: temperature at the maximum reaction rate [K]
t	: time [s]
w <sub>0</sub>	: initial sample mass [mg]
w <sub>f</sub>	: final sample mass [mg]
w <sub>t</sub>	: sample mass at time t [mg]
α	: degree of conversion
β	: heating rate [K/min]
ε	: voidage fraction

### REFERENCES

1. E. Salehi, J. Abedi and T. Harding, *Energy Fuels*, **23**, 3767 (2009).
2. ICO, *Coffee consumption in East and Southeast Asia: 1990-2012*. London: ICC 112-4[ICO Document], International Coffee Organization 2014.
3. S. Y. Oh, H. W. Hwang, H. S. Choi and J. W. Choi, *Fuel*, **153**, 535 (2015).
4. Q. Lu, X. L. Yang and X. F. Zhu, *J. Anal. Appl. Pyrol.*, **82**, 191 (2008).
5. S. Nanda, P. Mohanty, J. A. Kozinski and A. K. Dalai, *Eng. Environ. Res.*, **4**(3), 21 (2014).
6. J. P. Bok, Y. S. Choi, S. K. Choi and Y. W. Jeong, *Ren. Energy*, **65**, 7 (2014).
7. Y. S. Choi, S. K. Choi and Y. W. Jeong, *Env. Prog. Sust. En. J.*, **33**(4), 1405 (2014).
8. F. Abnisa, A. Arami-Niya, W. M. A. Wan Daud and J. N. Sahu, *Bioenergy Res.*, **6**, 830 (2013).
9. J. P. Bok, H. K. Choi, Y. S. Choi, H. C. Park and S. J. Kim, *Energy*, **47**, 17 (2012).
10. C. Wang, Z. Du, J. Pan, J. Li and Z. Yang, *J. Anal. Appl. Pyrol.*, **78**, 438 (2007).
11. E. Önal, B. B. Uzun and A. E. Pütün, *Energy Convers. Manage.*, **78**, 704 (2014).
12. J. D. Martínez, A. Veses, A. M. Mastral, R. Murillo, M. V. Navarro, N. Puy, A. Artigues, J. Bartroli and T. García, *Fuel Proc. Technol.*, **119**, 263 (2014).
13. X. Li, V. Strezov and T. Kan, *J. Anal. Appl. Pyrol.*, **110**, 79 (2014).
14. K. J. Kim and S. K. Park, *Korean J. Food Sci. Technol.*, **28**(2), 153 (2006).
15. R. Soysa, S. K. Choi, Y. W. Jeong, S. J. Kim and Y. S. Choi, *J. Anal. Appl. Pyrol.*, **115**, 51 (2015).
16. H. S. Choi, Y. S. Choi and H. C. Park, *Korean J. Chem. Eng.*, **27**(4), 1164 (2010).
17. J. E. White, W. J. Catallo and B. L. Legendre, *J. Anal. Appl. Pyrol.*, **91**, 1 (2011).
18. H. L. Friedman, *J. Polym. Sci. Part C: Polymer Letters*, **6**, 183 (1964).
19. M. R. B. Guerrero, M. M. D. S. Paula, M. M. Zaragoza, J. S. Gutiérrez, V. G. Velderrain, A. L. Ortiz and V. Collins-Martínez, *Int. J. Hydrogen Energy*, **39**(29), 16619 (2014).
20. Y. H. Park, J. Kim, S. S. Kim and Y. K. Park, *Bioresour. Technol.*, **100**, 400 (2009).
21. M. R. Othman, Y. H. Park, T. A. Ngo, S. S. Kim, J. Kim and K. S. Lee, *Korean J. Chem. Eng.*, **27**(1), 163 (2010).
22. H. H. Sait, A. Hussain, A. A. Salema and F. N. Ani, *Bioresour. Technol.*, **118**, 382 (2012).
23. J. Reina, E. Velo and L. Puigjaner, *Ind. Eng. Chem. Res.*, **37**, 4290 (1998).
24. D. Vamvuka, E. Kakaras, E. Kastanaki and P. Grammelis, *Fuel*, **82**, 1949 (2003).
25. M. Jeguirim, L. Limousy and P. Dutournie, *Chem. Eng. Res. Design*, **92**, 1876 (2014).