Pyrolysis kinetic study of homogenized waste plastic and date blend

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Abstract. Pyrolysis of high-density polyethelene (HDPE) and dried Dates blends are examined in this paper. There is abundance of HDPE and Dates waste available in Iran. Due to this factor, there are potentials to study these wastes in term of waste to energy conversion as feedstock in powerplants. In order to produce a quality fuel or feedstock by converting Dates and plastics waste through pyrolyzing, a proper analysing of the process kinetic parameters and the distribution of their activation energy (Ea) has been investigated. In this paper, three samples of HDPE and Dates blend with ratio of (1:3, 1:1 and 3:1) were utilized to study the thermal degradation of each blending sample using TGA analyser. Moreover, the Ea of HDPE and Dates blend was calculating using Friedman Method. The determined result for ratio of 1HDPE:3Dates is 60-67 kJ/mol, for 1HDPE:1Dates is 66-97 kJ/mol and for 3HDPE:1Dates is 131 kJ/mol. The higher ratio of plastic can increase the value of activation energy which require more energy for combustion in powerplant. Thus, the 1HDPE:3Dates is the best ratio which require lowest energy for combustion and by homogenizing the plastic with biomass we can increase the calorific value of the produce feedstock.

1. Introduction
Nowadays energy plays a significant role in the global economy. In the past decades in the world, biomass as an important renewable energy source, attracting more attention of researchers and companies. There are estimates that show certain fossil fuels, such as crude oil and natural gas related to members of the Organization of Petroleum Exporting Countries (OPEC), will be exhausted in 79 and 131 years, respectively and that average depletion times for world fossil fuel reserves such as of oil, coal and gas are approximately 35, 107 and 37 years, respectively. In addition, fossil fuels are the primary cause of greenhouse gas emissions, which are currently the most perilous threat to the environment. Total global carbon dioxide emissions in 2010 were more than 33.1 gigatons—33% more than in 2000 (24.8 gig tonnes) [1-4].

Global plastics production is currently estimated to be 300 million metric tons each year and is growing at a rate of 4% annually. The World Bank projects that 1.3 billion metric tons of municipal solid waste (MSW) is generated each year, besides this number is expected to grow to 2.2 billion metric tons per year (MTPY) by 2025. Around 10% of the total MSW produced (130 Million MTPY) is the composed of plastic. Since plastic waste virtually does not degrade, it persists for hundred years after they are dumped in the dumpsites. Thus, this accumulation of plastic products is serious threat to the prospect of the ecosystem in general and to the health of human society in particular [5-7].
A clear comprehension of biomass pyrolysis can offer ascent to a sensational improvement of biomass transformation process. Since pyrolysis is the initial step of biomass transformation, for example, gasification, liquefaction, carbonization, and ignition, its sound comprehension is noteworthy for the successful utilization of biomass. For engineering applications, information of the pyrolysis energy is fundamental for anticipating the pyrolysis conduct of biomass materials and their mixes.

Biomass is the solely renewable strength supply that can be converted into quite a few types of fuels such as liquid (bio-oil), stable (char), and gas with promising flexibility in manufacturing and advertising. It is estimated that biomass will contribute to average of 15% to 50% of the world’s primary energy consumption by 2050 [8-9]. Moreover, biomass as one of the world’s largest sustainable energy sources has plenty alternative energy resources existing in diverse forms all over the world and can be used to replace the conventional fossil fuels due to its availability, innumerable economic and environmental benefits since it is a carbon source with carbon dioxide, CO₂ neutrality. Co-pyrolysis is a safe and simple production process for high quality fuels since it does not require high-pressure hydrogenation, the hydrogen transfer can take place under ambient pressure conditions during the co-pyrolysis process.

This research aims to investigate the process kinetic parameters and the distribution of activation energy (Eₐ) of plastics and biomass blends. The co-pyrolysis process of biomass and plastic waste has been mentioned as an effective improving method that will not only increase the volume of oil produced but also improve its quality in terms of high calorific value because synthetic plastics are high carbon and hydrogen contents, with minimal oxygen, offering a relatively high heating value to conventional fossil fuels such as diesel and gasoline. When biomass and plastic are combined together, unlike the one decomposition staged observed when the materials were undergone pyrolysis alone, the pyrolysis of blends is characterized by 2 decomposition stages [9-10]. The type of co-pyrolysis of mixture and the percentages of the materials in the blend will affect the decomposition intensity. The first decomposition stage is mainly the decomposition of the biomass and slightly influenced by the plastic materials due to the reactions being below 64K for the blends. Plastics do not decompose at this temperature and only softens which can affect the mass and heat transfer at this temperature range. For the second decomposition stage, it is the combination of thermal degradation of the plastic material and biomass in the mixture. At this temperature range, lignin component of the biomass decomposes [9, 11-13].

2. Methodology

2.1. Sample preparation
Both HDPE plastic-dried Dates and HDPE plastic-Dates samples grinded into small pieces with the size of 250 μm and weight range from 15 mg to 20 mg. The weight ratio of plastic and Dates blend are shown in table below [14].

| Plastics and Dates blend samples | Ratio          |
|---------------------------------|---------------|
| HDPE                            | 1             |
| HDPE and Dates Blends           | (HDPE): 3(Dates) |
| HDPE and Dates Blends           | (HDPE): 1(Dates) |
| HDPE and Dates Blends           | 3(HDPE): 1(Dates) |

2.2. Thermogravimetric analysis (TGA)
Thermogravimetric analysis (TGA) is an entrenched strategy in the assurance of the weight reduction qualities and its related response energy. There are 4 main parameters involve in investigating the thermal degradation process. The parameters are heating rates, temperature, mass loss and the time taken for each sample to remove its moisture, volatile and ash content. The experiment is conducted with the heating rate of 10°C/min in inert atmosphere for both HDPE plastic sample and dried dates sample. This is based on the standard heating rate selection used by researcher in the previous study [15]. As indicated
by the ISO Standards, intrinsic moisture is resolved at temperature in the vicinity of 105°C and 110°C for 1 hour, volatile content at 900°C for 7 minutes, and ash remains at 815°C for 3 hours. The settled carbon is computed by the contrast between moisture, volatile and ash content [16-17].

2.3. Kinetic model (Friedman Method)
Friedman method kinetic model is used to calculate the Arrhenius parameters and also to determine of the activation energy and the pre – exponential factor. The method used to determine differences in data obtained across multiple sets. The Friedman method is classified under iso – conversional method with the usage of differential equation. It can be stated that the iso – conversional method is one of the reliable methods to calculate the kinetic parameters such as activation energy and pre – exponential factor.

Friedman method is the most used method for the conversion. Moreover, ln \[ \frac{\beta da}{dt} \] to 1/T the suitable method which can used the least square method is used to fit the relationship between the rate increase in temperature and temperature where the reaction of mechanism can be avoided. Thus, the activation energy, \( E_a \) can be obtained from the slope and the pre – exponential factor, \( A \) can be estimated from the intercept from the Y – axis. This is the reason why the Freidman method is considered as free – model method [5, 13, 18].

Arrhenius Equation:
\[
\frac{d\alpha}{dt} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} (1-\alpha)
\]  
Friedman Method:
\[
\ln \left[ \frac{\beta da}{dt} \right] = \ln[f(a)] \frac{E_a}{RT} 
\]
Intercept:
\[
\ln \left[ \frac{\beta da}{dt} \right] \text{against } \frac{1}{T}
\]

3. Results and discussion

3.1. Proximate analysis
The proximate analysis for Dates sample with the size of 250 μm pyrolysis was done under the condition of 10ºC/min heating rate and 25ml/min of \( N_2 \) flowrate. The results of the analysis were represented by the graph in Figure 1.

![Decomposition curve for Dates sample.](image)

Based on the graph, the first decomposition of dried Dates occurs at the temperature of 100ºC while the second decomposition occurs at the temperature of 200ºC to 310ºC and the third decomposition occurs between the temperature of 310ºC to 350ºC. Based on these decomposition temperatures, the dried Dates sample experienced a moisture weight loss of 11.69%, volatile weight loss of 41.63% and ash loss of 3.11%.
Figure 2. Decomposition curve for plastic sample.

From Figure 2, it can be seen that the HDPE sample only undergoes a single stage of thermal decomposition at the temperature range of 400°C to 500°C compared to Dates sample which went to triple stages of thermal decomposition. This is because the moisture content presence in plastic is theoretically lower when compared to biomass. Hence, resulting in a sole stage of thermal decomposition. Based on the decomposition range, it was found that the moisture content of the individual HDPE plastic is 0.79 %, volatile content is 80.66 % and ash content of 9.80 %.

Figure 3. Decomposition curve for 1 HDPE: 3 Dates sample.

Based on Figure 3, it can be seen that the sample went through two stages of decomposition. The first decomposition takes place at the temperature range of 300°C to 350°C while the second decomposition occurs between the temperatures of 350°C to 420°C. The initial weight of the sample was 3.58 mg and ended with a weight of 0.28 mg. From the weight difference, the sample experienced a weight loss of 93.92% and have a 6.08% of residue. The result indicates, that the sample had a moisture loss of 7.13%, volatile loss of 72.03% and left with a final weight of 6.08% of ash.
Based on Figure 4, it can be observed that the sample undergoes two stages of decomposition. The first decomposition takes place at the temperature range of 300°C to 350°C while the second decomposition occurs between the temperatures of 350°C to 435°C. The initial weight of the sample was 1.27 mg and ended with a weight of 0.29 mg. From the weight difference, the sample experienced a weight loss of 94.21% and have a 5.79% of residue. This result denotes that the sample had a moisture of 8.21%, volatile of 74.85% and 8.69% of ash.

Based on Figure 5, it shows that the sample went through a single stage of thermal decomposition. The decomposition takes place at a temperature range between 350°C to 445°C. The result is poles apart from the first and second sample which undergoes a twofold stage of thermal decomposition. This is due to the high content of plastic sample in the mix causing the pattern of the graph to be similar as the pattern of the graph of individual plastic sample.

A summary of the proximate analysis for all individual HDPE, individual dried Dates as well as HDPE and dried Dates blends samples are shown in Table 2 and has been compared with different types of biomass and Plastic sample. Result proved that by mixing biomass with plastic samples we can get higher volatile matter, less ash and moisture content and these can be considered as a better feedstock compare to 100% biomass fuels.
Table 2. Proximate analysis for individual HDPE, individual Dates, HDPE and Dates blends samples.

| Samples                  | Moisture (%) | Volatile (%) | Ash (%) |
|--------------------------|--------------|--------------|---------|
| HDPE                     | 9.80         | 80.66        | 0.79    |
| Dried Dates              | 11.69        | 41.63        | 3.11    |
| 1 HDPE:3 Dates           | 7.13         | 72.03        | 6.08    |
| 1 HDPE:1 Dates           | 8.21         | 74.85        | 5.79    |
| 3 HDPE:1 Dates           | 8.27         | 84.14        | 3.21    |
| Hazelnut Shell [18]      | 10.94        | 68.98        | 0.71    |
| Cotton Stalk [20]        | 7.46         | 64.92        | 5.52    |
| Polystyrene [21]         | 3.30         | 95.08        | 4.02    |

3.2. Activation energy

The required energy which starts the reaction or amount of energy available in chemical system for the process to take charge is normally called as activation energy. This will occur when the particles are moving, and the movement is the one takes the energy. Moreover, heat energy is the source to push the activation energy reaction from the surrounding to speed up the motion of the molecules, heat energy plays an important aspect where increasing the frequency and force when collide with each other. For this to occur, the temperature should be high.

Figure 6. Activation energy slope for 1(HDPE) and 3 (Dates) Sample.

Figure 7. Activation energy slope for 1 (HDPE) and 1 (Dates) Sample.
Figure 8. Activation energy slope for 3 (HDPE) and 1 (Dates) sample.

The activation energy of HDPE shows that it require high amount of energy to start the combustion, and this number for biomass is much lower. Using high amount of energy is an issue for combustion which can be solve by mixing the HDPE with biomass to get the average amount of energy to start the combustion. However, for the individual sample of plastic and Dates, the Ea value calculated using the Friedman method is closely identical with the value in other studies. Biomass sample went through triple stages of thermal decomposition. While, all of the plastic sample went through a single stage of thermal decomposition. Nevertheless, when the plastic sample was interblend with the biomass sample, a two stage of thermal decomposition emerged. All homogenized samples undergo the Thermogravimetric analysis (TGA) to obtain the activation energy. Based on previous study [5], the activation energy for HDPE is 225.38 kJ/mol and this number for the biomass sample (Dates waste) is 41.73-43.28 kJ/mol. Due to the corresponding DTGA curve and activation energy slope graph, the activation energy range for 1HDPE:3Dates Sample is 43.28-41.73 kJ/mol. The activation energy for the ratio of 1:1 is 65.78-97.18 kJ/mol and the range for the ratio of 3HDPE:1Dates is 131.28 kJ/mol. The activation energy values for all samples has been tabulated as shown in Table 3.

Table 3. Activation energy (Ea) of HDPE and Dates blends by Redfern Method.

| Sample          | Temperature(°C) | Ea (kJ/mol) | $R^2$ |
|-----------------|-----------------|-------------|-------|
| HDPE            | 415-465         | 225.38      | 0.98  |
| Dates           | 50-70           | 43.28       | 0.99  |
|                 | 313-350         | 41.73       | 0.98  |
| 1HDPE:3Dates    | 300-330         | 60.88       | 0.90  |
|                 | 353-403         | 66.67       | 0.93  |
| 1HDPE:1Dates    | 300-335         | 65.78       | 0.93  |
|                 | 353-400         | 97.18       | 0.97  |
| 3HDPE:1Dates    | 350-420         | 131.28      | 0.97  |
| HDPE [21]       | 440-550         | 236.2       | 0.99  |
| 1HDPE:1SW [21]  | 286-405         | 128         | 0.97  |
| Newspaper       | 310-370         | 142.3       | 0.99  |

Basically high activation energy will not react without any input of energy. For instance, combustion of coal will release energy, but the rate of reaction is zero in room temperature. Practically, it would not be good if the coal combust spontaneously because the loss of energy due to fast reactions. Therefore, once there is input of energy such as ignition, it’s enough energy to provide the molecules to overcome the barrier releasing energy. By increasing the percentage of biomass, result shows that we reduced the...
activation energy. By adding 25% biomass the activation energy from 236.2 kJ/mol, decreased to 131.28 kJ/mol and by adding 50% of biomass the activation energy decreased to 97.18 kJ/mol. By mixing 75% of biomass and 25% of plastic the activation energy decreased to 60.88 kJ/mol. Reducing the activation energy means, using less energy to start the combustion and this is an important matter for a fuel to be consider as a good feedstock for energy recovery.

4. Conclusion
In this research, the potential of mixed plastic and agricultural waste as feedstock for energy recovery is studied. The activation energy of three different ratios of samples using Thermogravimetric analysis (TGA) has been found based on the degradation curve and DTGA curve. The percentage of moisture and ash content and volatile matter (proximate analysis) had been calculated based on conducted TGA result. Based on obtained results, the high-density polyethylene (HDPE) has high activation energy compare to the Date waste however, by mixing these two materials, the required energy will reduce. The results show, the activation energy range for 1HDPE:3Dates Sample is 43.28-41.73 kJ/mol, the range for the ratio of 1:1 is 65.78-97.18 kJ/mol and the range for the ratio of 3HDPE:1Dates is 131.28 kJ/mol. The results show when the amount of HDPE increase, the value of activation energy will rise. The conducted experiment proved that the potential use of homogenized sample as feedstock for energy recovery based on low energy required to start the reaction in combustion is in the order of 1HDPE:3Dates, 1:1 and 3HDPE:1Dates. On the other hand, based on the proximate analysis, the potential homogenized sample as feedstock for energy recovery, due to low amount of ash and moisture content and high volatile matter, follows the order of 1HDPE:3Dates, 1:1 and 3HDPE:1Dates. Based on the result, the ratio of 1:1 is found as the better source of energy recovery because of the average energy require as activation energy, amount of moisture content, ash content and volatile matter.

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