Effect of Sodium Boron Hydride (NaBH₄) on Waste Polyethylene Terephthalate Pyrolysis

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Abstract. Polyethylene terephthalate, which is used in many applications today, is very important in terms of nature and source in order to ensure recycling by appropriate methods after use. Because polyethylene terephthalate is a durable and long-lasting thermoplastic which is resistant to many environmental influences. Recovering residual plastics has become mandatory. In this study, the conversion of waste plastic to a new liquid fuel by polyethylene terephthalate (PET) pyrolysis method was investigated. Sodium boron hydride (NaBH₄) was used as both catalyst and hydrogen donor in the pyrolysis experiments. Pyrolysis experiments were carried out in a batch reactor under catalytic and non-catalytic conditions, reaction time of 15-90 minutes, reaction temperature of 325-425 °C, solid/solvent ratio of 1/4 and initial nitrogen gas pressure of 20 bar. According to the results obtained, the most suitable reaction temperature was found to be 375-425 °C and the reaction time was 30 minutes. At the reaction times of 30 minutes, the maximum total conversion in non-catalytic conditions of waste polyethylene terephthalate samples was 53.1% at 400 °C reaction temperature and the highest oil + gas yield was 43.7% at 425 °C reaction temperature. In the pyrolysis of polyethylene terephthalate samples in the presence of sodium boron hydride, the maximum total conversion was 55.3% at 400 °C reaction temperature and the highest oil + gas yield was 44.6% at 425 °C reaction temperature. As a result, it can be argued that sodium boron hydride used in pyrolysis experiments of waste polyethylene terephthalate acts as both catalytic and hydrogen donor.

1. Introduction
PET has high resistance to most solvents, weak acids and bases among thermoplastics as well as strength, gloss, high impact strength and hardness. Because of these properties, it is a preferred packaging material in many applications [1-4]. It is also widely used in areas such as garments, pillows, sheets, carpets, ropes, hoses and cords of fibers produced by melt spinning from PETs [5]. As a result of the increase in the usage area of PETs at day by day, the amount of waste discharged to nature increases in the same way. The conversion of these valuable wastes into valuable products by appropriate methods is important for both natural resources and the environment. Problems such as recycling, storage and incineration of plastic wastes made it necessary to convert them into chemical raw materials and to obtain energy by chemical methods. The transformation of plastic wastes into gas and liquid fuels and petrochemical raw materials is seen as an alternative option in terms of both energy and raw materials and environment [6, 7]. Pyrolysis, which is one of the waste plastic recycling methods,
is one of the most promising technologies of today [8]. As a result of pyrolysis process, char, liquid and gas products are obtained [2, 8].

2. Experimental Section
2.1. Materials

During the liquefaction experiments, Sodium Boron hydride (NaBH₄) (Merck), tetralin (98%, Sigma Aldrich), hexane (extra pure, Merck), toluene (GR ACS ISO, Merck), nitrogen gas (N₂ gas) and tetrahydrofuran (THF) (Merck) were used as the consumption material and a stirring and heating, batch reactor (Parr, 500 ml) was used.

2.2. Procedure

In this study, the effect of reaction temperature, reaction time and NaBH₄ on the pyrolysis efficiency investigated by directly using liquefaction method in pyrolysis experiments. The PET particle size, the initial pressure, and the solid/solvent ratio were fixed and the pyrolysis process was carried out in inert atmosphere and non-catalytic/catalytic conditions. The pyrolysis experiments conditions are given in Table 1. The optimum PET pyrolysis parameters by the liquid product efficiency were defined after the experiments made. The optimum parameters in the liquefaction of PET were taken as a base; and the experiment conditions to be made for the optimization of conditions in the joint liquefaction of the reaction temperature and reaction time were determined. Analysis of the experiments using PET samples were given in Table 2 and 3, the pyrolysis experiments were made according to the flow chart showing in Figure 1.

### Table 1. The liquefaction experiments conditions.

| Exp. no | PET (g)  | Temp (°C) | Time (min.) | Catalyst concentration (NaBH₄, wt. %) |
|---------|----------|-----------|-------------|-----------------------------------|
| 1       | 30.003   | 325       | 30          | 3                                 |
| 2       | 30.000   | 350       | 30          | 3                                 |
| 3       | 30.000   | 375       | 30          | 3                                 |
| 4       | 30.005   | 400       | 30          | 3                                 |
| 5       | 30.002   | 425       | 30          | 3                                 |
| 6       | 30.002   | 325       | 30          | ---                               |
| 7       | 30.002   | 350       | 30          | ---                               |
| 8       | 30.002   | 375       | 30          | ---                               |
| 9       | 30.002   | 400       | 30          | ---                               |
| 10      | 30.002   | 425       | 30          | ---                               |
| 11      | 30.005   | 400       | 15          | 3                                 |
| 12      | 30.000   | 400       | 60          | 3                                 |
| 13      | 30.000   | 400       | 90          | 3                                 |
Table 2. The proximate analysis of the PET samples (wt. % as used).

| Sample name | Moisture | Ash | Volatile matter | Fixed carbon* |
|-------------|----------|-----|-----------------|---------------|
| PET         | 0.3      | 0.0 | 88.3            | 11.4          |

* By difference

Table 3. The ultimate analysis of PET samples (wt. % daf).

| Sample name | C    | H    | N    | S    | O*   |
|-------------|------|------|------|------|------|
| PET         | 61.86| 4.38 | 0.0  | 0.0  | 33.76|

* By difference

Figure 1. Flow chart of the pyrolysis experiments.

3. Results and discussions
In all pyrolysis experiments carried out under both catalytic and non-catalytic conditions, the temperature change over time was as given in figure 2-3 and the pressure changed proportional to the temperature (Figure 4-5). As can be seen in Figure 4-5, during the reaction time, the pressure was obtained in the range of 70-95 bar.
Figure 2. The change in the temperature of the reactor in the non-catalytic conditions (reaction temperature 425 °C, reaction time 30 minutes).

Figure 3. The change in the temperature of the reactor in the catalytic conditions (reaction temperature 425 °C, reaction time 30 minutes).

Figure 4. The change in the pressure of the reactor in the non-catalytic conditions (reaction temperature 425 °C, reaction time 30 minutes).
Char yield and total conversion rates obtained in catalytic and non-catalytic conditions are given in Table 4. As can be seen from Table 4, the carbon and hydrogen contents of the chars obtained in catalytic conditions are higher than in non-catalytic conditions. Under the same conditions, the carbon content was 50.11% and the hydrogen content was 3.31% in catalytic conditions (Experiment: 4), while the carbon content was 57.62% and hydrogen was 3.71% in non-catalytic conditions (Experiment: 9). Under the same conditions, the content of char samples in the catalytic condition (Experiment:4) was the C 50.11% and the H 3.31%, whereas they (Experiment:9) was C 57.62% and H 3.71% in the non-catalytic condition. As a result, in PET pyrolysis, sodium boron hydride had an effect on liquid+gas yield and total conversion. According to these results, sodium boron hydride had a catalytic effect on the total conversion of liquid + gas obtained from pyrolysis of waste PET and total conversion.

Table 4. The ultimate analysis of char samples (wt. % daf).

| Exp. no | Catalyst concentration (NaBH₄, wt. %) | Reaction time (min.) | Temp. (°C) | C   | H   | O* |
|--------|-------------------------------------|----------------------|-----------|-----|-----|----|
| 1      | 3                                   | 30                   | 325       | 60.13 | 4.70 | 35.12 |
| 2      | 3                                   | 30                   | 350       | 59.22 | 4.65 | 36.10 |
| 3      | 3                                   | 30                   | 375       | 58.67 | 4.38 | 36.94 |
| 4      | 3                                   | 30                   | 400       | 50.11 | 3.31 | 46.57 |
| 5      | 3                                   | 30                   | 425       | 51.55 | 3.22 | 45.19 |
| 6      | ---                                 | 30                   | 325       | 63.70 | 4.55 | 31.69 |
| 7      | ---                                 | 30                   | 350       | 63.87 | 4.51 | 31.61 |
| 8      | ---                                 | 30                   | 375       | 61.54 | 4.13 | 34.29 |
| 9      | ---                                 | 30                   | 400       | 57.62 | 3.71 | 38.64 |
| 10     | ---                                 | 30                   | 425       | 57.56 | 3.53 | 38.89 |
| 11     | 3                                   | 15                   | 400       | 55.80 | 3.84 | 40.34 |
| 12     | 3                                   | 60                   | 400       | 47.49 | 3.36 | 49.15 |
| 13     | 3                                   | 90                   | 400       | 51.22 | 3.12 | 45.65 |

* By difference
As can be seen in Table 5, the total conversion increased from 15.2% to 55.3% in catalytic conditions as a result of increasing the reaction temperature from 325 °C to 400 °C, while there was a partial decrease after 400 °C. As a result of increasing the reaction temperature from 325 °C to 375 °C, PAS + AS yield increased from 8.3% to 34.1%, oil + gas yield increased from 6.9% to 9.2%, after 375 °C PAS + AS yield decreased to 7.2% and oil + gas yield increased to 44.6%. Considering the conversion mechanism of PET under catalytic conditions, it increases the light products (oil + gas) due to increasing conversion of decomposition products in the high reaction temperature. Under non-catalytic conditions, the total conversion increased from 9.4% to 53.1% as a result of increasing the reaction temperature from 325 °C to 425 °C (Table 5). In both catalytic and non-catalytic conditions, the total conversion at low reaction temperatures was very low, but increased significantly at high reaction temperatures (375 °C and above).

Total conversion and liquid + gas yields can be said to be 30 minutes (Table 6 and Figure 7) and the reaction temperature is 400 °C (Table 5) under catalytic conditions. In non-catalytic conditions, the highest total conversion was obtained at 425 °C and 30 min. However, as can be seen in the Figure 6, based on oil + gas yield, it can be asserted that the appropriate reaction temperature is 425 °C under both catalytic and non-catalytic conditions (Table 5).

| Exp. no | Sample amount (wt. as used) | Catalyst concentration (NaBH₄, wt. %) | Time (minute) | Temp. (°C) | Char yield (wt., %) | Total conversion (wt., %) | PAS + AS (wt., %) | Oil + Gas (wt.*, %) |
|---------|-----------------------------|----------------------------------------|---------------|-------------|----------------------|-------------------------|------------------|-------------------|
| 1       | 30.00                       | 3                                      | 30            | 325         | 84.8                 | 15.2                    | 8.3              | 6.9               |
| 2       | 30.00                       | 3                                      | 30            | 350         | 75.0                 | 25.0                    | 12.1             | 12.9              |
| 3       | 30.00                       | 3                                      | 30            | 375         | 56.7                 | 43.3                    | 34.1             | 9.2               |
| 4       | 30.00                       | 3                                      | 30            | 400         | 44.7                 | 55.3                    | 26.7             | 28.6              |
| 5       | 30.00                       | 3                                      | 30            | 425         | 48.2                 | 51.8                    | 7.2              | 44.6              |
| 6       | 30.00                       | ---                                    | 30            | 325         | 90.6                 | 9.4                     | 9.3              | 0.1               |
| 7       | 30.00                       | ---                                    | 30            | 350         | 84.7                 | 15.3                    | 14.2             | 1.1               |
| 8       | 30.00                       | ---                                    | 30            | 375         | 66.5                 | 33.5                    | 29.4             | 4.1               |
| 9       | 30.00                       | ---                                    | 30            | 400         | 49.5                 | 50.5                    | 31.8             | 18.7              |
| 10      | 30.00                       | ---                                    | 30            | 425         | 46.9                 | 53.1                    | 9.3              | 43.7              |

* By difference; PAS (Preasphaltene); AS (Asphaltene)
Figure 6. The effect on the oil+gas yield with reaction temperature.

Table 6. The change on the total conversion with reaction time.

| Exp. no | Sample amount (wt. as used) | Catalyst concentration (NaBH₄, wt. %) | Time (minute) | Temp. (°C) | Char yield (wt., %) | Total conversion (wt., %) |
|---------|-----------------------------|--------------------------------------|---------------|------------|---------------------|--------------------------|
| 11      | 30.01                       | 3                                    | 15            | 400        | 58.6                | 41.4                     |
| 4       | 30.01                       | 3                                    | 30            | 400        | 44.7                | 55.3                     |
| 12      | 30.01                       | 3                                    | 60            | 400        | 49.1                | 50.9                     |
| 13      | 30.00                       | 3                                    | 90            | 400        | 48.3                | 51.7                     |

Figure 7. The change on the total conversion with reaction time.

4. Conclusions
It has been observed that the use of sodium boron hydride as catalyst and hydrogen donor increases both total conversion and oil + gas yields for the conversion of waste PET to suitable products by pyrolysis. According to the results obtained, it can be said that the appropriate reaction temperature is 425 °C and the reaction time is 30 minutes.
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