Methane Synthesis from Automotive Paint Sludge via Microwave Assisted Pyrolysis

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Abstract. Methane gas, which has one atom of carbon and four atoms of hydrogen, is a valuable energy resource, which can be used in the energy sector. The purpose of this research work is to identify methane synthesis from Automotive Paint Sludge (APS) using microwave assisted pyrolysis. APS is known as a hazardous waste since it contains various chemicals that categorized as heavy metals and toxic substances. A modified conventional kitchen microwave was used to pyrolise the APS. The microwave was set with the power level of 600 W and 50 minutes radiation time. Through the experiment, pyrogas was collected into tedlar bag and was analysed using Gas Chromatography with Flame Ionization Detector (GC-FID). Results from the GC-FID were shown that the retention time of 3.3583, 3.2733, and 3.2267 min are proved to be methane gas. The results obtained are resembled with the results from the literature. This indicates methane gas was presented in the pyrogas of pyrolysis of APS and there is a possibility of producing methane gas. The research study suggests that it is possible to synthesize methane gas from the APS via microwave assisted pyrolysis, and in the meantime reduce the volume of APS in the landfill.

1. Introduction

The number of vehicles produced has become increasing in recent years due to the rising in market demand caused by the development in the modernization and population. Salihoglu and Salihoglu (2016) mentioned that the demand for vehicles production has been increasing at a constant rate [1]. Unfortunately, with the increasing demand for vehicle production, it will lead to the increasing of APS in the landfill. Automotive Paint Sludge (APS) is a waste paint resulting from the automotive manufacturing industry. Paint sludge is waste water containing the mixture of over sprayed paint and water. The over sprayed paint is resulted from the paint that not reaching the target in a painting by spraying method while the water in the sludge paint resulted from the circulating water that used to wash the overspray and collected in a sludge pit [2]. APS contain various chemicals and has been classified as hazardous waste. According to Gautam, Bundela and Murumkar (2010), APS contains heavy metals and other toxic substances, due to which has high pollution potential [3]. One way to overcome this problem is to use APS in order to produce valuable products. APS has been identified as one of the option of fuel production obtained from microwave assisted pyrolysis techniques [4]. According to Januri et al. (2015), APS contain calorific value about 22.6 MJ/kg, which indicate that it is a good potential for the future alternative fuel which can produce solid, liquid and gas product [5]. Table 1 shows the characteristics of APS. Rahman et al. (2015) studied on the yield of microwave
pyrolysis of APS by using microwave absorber [6]. However, although APS has been proven very useful in producing fuel, little attention has been paid to the production of methane gas from pyrolysis of the APS using microwave.

| Analysis Parameters                  | Values     |
|--------------------------------------|------------|
| Calorific value                      | 22.6 MJ/kg |
| Melting point                        | 376.56 °C  |
| Enthalpy of melting                  | 66.7 J/kg.K|
| Ash                                  | 2.9 wt.%   |
| Moisture                             | 2.4 wt.%   |
| Volatile matter                      | 75.9 wt.%  |
| Fixed carbon                         | 3.2 wt.%   |
| Carbon                               | 38 wt.%    |
| Hydrogen                             | 10 wt.%    |
| Ultimate analysis                    |            |
| Nitrogen                             | 9 wt.%     |
| Sulfur                               | 1 wt.%     |
| Oxygen                               | 42 wt.%    |

Chemical composition: \( C_{38}H_{10}N_{9}SO_{42} \)

Methane is a gaseous form in its natural state with the chemical formula \( \text{CH}_4 \) and is the simplest component in alkane chemical class. Howarth (2011) stated that methane gas was the main component and is the primary components of natural gas [7]. Zhang, Liang and Harpalani (2016) produced methane from bituminous coal through biogasification process [8]. Methane also can be produced from the digestion of glucose and sludge using microbial electrolysis cell assisted anaerobic digestion systems [9]. Zou et al. (2016) conducted a research in producing methane production from pretreatment of food waste with high voltage pulse discharge using multi-needle-to-plate reactor [10]. According to Córdoba et al. (2016), methane can be produced from spent populus sawdust obtained from the cultivation of \( \text{Gymnopilus pampeanus} \) [11]. Many researchers doing research in the production of methane since it is important to produce methane besides depending on the natural gas because natural gas will deplete in the future.

Microwave is a heating equipment that use short waves of electromagnetic energy that increases the kinetic energy of water dipoles to its boiling point very quickly [12]. Chan et al. (2013) evaluated the anaerobic biodegradability of microwave pre-treated dairy manure in the methane production [13]. Jackowiak, Bassard, Pauss, and Ribeiro (2011) performed a research in microwave pre-treatment of wheat straw for methane production [14]. Marin, Kennedy, and Eskicioglu (2010) investigated on the methane production from a model kitchen waste using high temperature and pressure microwave irradiation [12]. Pyrolysis is the thermal decomposition process occurring in the absence of oxygen [15]. The product produced will be varied, depend on the pyrolysis method, residence time, temperature to which the biomass is exposed and the characteristics of the biomass itself. Bucko et al. (2014) also stated that pyrolysis produced four main end products include biochar, wood vinegar (from bio oils), creosote (from bio oils) and electricity (methane gas from pyrogas) [16]. The present research work proposes to identify methane synthesis from automotive paint sludge using microwave assisted pyrolysis. This method forms a novel for methane synthesis where the pyrolysation of APS significantly reduced the volume of APS in landfills and in the meantime produces valuable methane gas.
2. Experimental

2.1 Materials

The experiment involved the pyrolysis of APS via microwave and analysing the pyrogas obtained to identify the existence of methane gas via Gas Chromatography with Flame Ionization Detector (GC-FID). The sample of APS was collected from an automotive manufacturer industry in Selangor Darul Ehsan, Malaysia. The collected APS was placed in a covered container to avoid from any contamination during storage. Pure methane gas (high purity of 99.99 %) was purchased from Pure Dimension Enterprise, Malaysia and was used for comparison purpose.

2.2 Microwave assisted pyrolysis of APS

Prior to the pyrolysis process of APS, 200 g of APS and 20 g of activated carbon, which act as microwave absorber was placed in a quartz reactor before placing it inside the modified conventional kitchen microwave. The microwave was set with the power level of 600 W and 50 minutes radiation time. Nitrogen gas was purged into to microwave for 20 minutes before pyrolysis process and was continued flowing throughout the experiment to evacuate the air in the microwave and create nitrogen atmosphere. The microwave run was operated for 50 min. At 20, 30 and 40 minutes, pyrogas were collected and were stored into three different tedlar bags. After microwave had reached the radiation time of 50 minutes, the microwave was switched off.

2.3 Analysis

The collected pyrogas and pure methane gas were then analyzed using GC-FID according to the Standard practice for analysis of reformed gas by gas chromatography, American Society for Testing and Materials (ASTM) International, ASTM D1946 - 90(2015)e1 [17]. Table 2 shows the operating conditions of the GC-FID.

| Table 2. Operating Conditions of Gas Chromatography with Flame Ionization Detector Used [18]. |
| Parameter | Condition |
|------------|-----------|
| Oven temperature | 60 °C (Ramp rate 22 °C / min) |
| Detector temperature | 250 °C |
| Injector temperature | 150 °C |
| Injection volume | 1 mL |
| Carrier and make up gas with flow rate | Nitrogen, 2 mL/min |
| Hydrogen flow | 48 mL/min |
| Air flow | 500 mL/min |

3. Result and Discussion

In this research study, pyrogas was obtained from the pyrolysis of the APS using microwave. The results obtained from GC-FID were compared with pure methane gas. Table 3 shows the retention time of the GC-FID chromatogram of the pyrogas and pure methane gas.

| Table 3. Retention Time of the Gas Chromatography with Flame Ionization Detector Chromatogram of the Pyrogas and Pure Methane Gas. |
| Sample | Retention time (min) | Area (Counts) |
|----------|---------------------|---------------|
| Sample 1: Pyrogas taken at 20 min of radiation time | 3.3583 | 208684 |
| Sample 2: Pyrogas taken at 30 min of radiation time | 3.2733 | 1356719 |
| Sample 3: Pyrogas taken at 40 min of radiation time | 3.2267 | 2045462 |
| Sample pure methane gas | 2.8467 | 18132170 |
As can be seen, all three samples, which were taken in 20 minutes, 30 minutes, and 40 minutes of radiation time, have comparable retention time. This result is consistent with the result obtained by Wang (2010) where the retention time of methane gas obtained from the analysis of greenhouse gas standards was 3.314 minutes [18]. The results obtained in this research study also merge with the results obtained by Gedam and Regupathi (2012) in which the retention time of methane gas obtained from the analysis of syngas from municipal solid waste was 3.40 minutes [19]. To the degree that, Tipler (2010) also reported that the retention time of methane gas was 3.50 minutes, which also pursuant to other results [20]. However, the retention time of all three samples was not consistent with the retention time of pure methane gas. Pure methane gas has retention time earlier than those of the three samples, Wang (2010) and Gedam and Regupathi (2012) [18, 19]. This is due to the sample of pure methane gas used was high purity (99.99 %).

The peaks can be seen clearly in Figure 1, which shows the GC-FID chromatogram of the pyrogas and pure methane gas. The figure shows that the peak of all three samples lies under the peak of the pure methane gas. The pure methane gas has a width peak compared to those of the three samples because the pure methane gas used is a high purity gas with 99.99 %, while those of the three samples was obtained from pyrogas which has not purity as high as the pure methane gas. However, it was proved that the peaks existed in the GC-FID chromatogram of the pyrogas was methane gas whether it’s taken during 20 minutes, 30 minutes or 40 minutes of radiation time. Figure 2 shows comparison of the GC-FID chromatogram of the pyrogas and pure methane gas. As can be seen, even though pure methane gas has early retention time compared to those of the three samples, pure methane gas has a width peak compared to others.

![GC-FID chromatogram of the pyrogas and pure methane gas](image)

**Figure 1.** Gas Chromatography with Flame Ionization Detector Chromatogram of the Pyrogas and Pure Methane Gas.
4. Conclusion
In summary, retention time of 3.3583, 3.2733, and 3.2267 min obtained from the GC-FID of 20, 30 and 40 minutes radiation time of APS pyrolysis are proved to be methane gas. Thus, methane gas has been shown to be present in the pyrogas obtained from the pyrolysis of APS via microwave. Therefore, the research study has presented a novel technique for methane synthesis from APS via microwave assisted pyrolysis, and at the same time reduces the volume of APS in the landfills.

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