Hydrogen Production VIA Polyoxymethylene Degradation using Copper Nanocatalysts

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Abstract

Polyoxymethylene (POM) is an engineering thermoplastic. Formaldehyde is the monomer unit of this polymer. Depolymerization of POM occurs at 100°C and yields formaldehyde whereas thermal degradation occurs at 270°C. During thermal degradation, POM splits into carbon dioxide, water and formic acid. It has been proved that formaldehyde can be used as hydrogen source, when metallic nanoparticles are used as catalysts under particular parameters. In this experiment a trial has been made to produce hydrogen using POM scrape material. POM is used as formaldehyde source and copper nanoparticle is used as catalyst to produce sodium formate and hydrogen. Water is used as solvent for formaldehyde. Depolymerization is done with water at 100°C. The quantity of hydrogen produced is calculated based on sodium formate assay and statistical analysis. Sodium formate in different weights is taken for assay to measure precision, correlation coefficient and regression analysis.

Keywords: Polyoxymethylene, Depolymerization, Copper nanocatalysts, Hydrogen

1. Introduction

Hydrogen production is a costly affair so far. But it is mandatory to produce more hydrogen in future as an alternative source of natural fuel resources. Many investigations are going on to make hydrogen fuel cells in cost effective methods. It is understood that if hydrogen can be produced for low rates, automatically the price of Fuel cells will be reduced.

In this article, cost effective method of producing hydrogen, using polyoxymethylene (POM) scrape materials is presented. A meticulous literature study was made to incorporate a new idea on hydrogen production followed by a detailed account of the experiments and analysis.

1.1. What is POM?

Polyoxymethylene (commonly referred to as POM and also known as polyacetal or polyformaldehyde) is an engineering thermoplastic used in precision parts of machines that require high stiffness, low friction and excellent dimensional stability. Since POM is sensitive to many factors like acid, alkali,
radiation and heat, it is considered as one of the easily degradable polymers. The process of polymer degradation is a change in the properties like colour, tensile strength and other properties.

### 2. Previous Research

POM is a useful engineering polymer that has some structural and physical characteristics, favourable for making some esthetic orthodontic brackets. Robert P Kusy (2005), made a study to establish a thermal characteristic of POM brackets and the chemical by products released during thermal analysis, of POM brackets. During heating and mechanical abrasion, POM brackets produced formaldehyde gas [1]. In an experiment by Krzysztof German (2008) on comparison between the mass of the sample and the mass of collected products, POM decomposes thermally mainly as formaldehyde [2].

Polymeric materials change their properties during processing and recycling which is considered as salient feature. Polymeric chain damage mechanisms are initiated by temperature, shear or UV-light leading to dissociation. As a further consequence it may lead to failure of the component. Different methods of degradations of POM are thermo-mechanical, thermo-oxidative and photo-oxidative. It is well known that homopolymers and copolymers undergo degradation in different ways due to their specific chemical structure. Thermo Gravimetric Analysis (TGA) indicates a random scission of the main chain as the initiation mechanism of degradation [3]. The degradation of polyoxymethylenes under different conditions takes place essentially through five reactions; viz. (i) depolymerisation, starting on both ends of the polymer chain, (ii) autooxidative fission, (iii) decomposition by secondary products of the polymer chain, (iv) thermal degradation and (v) hydrolysis and acidolysis [4].

Kern (1967) defines that degradation reactions found in POM-homopolymers are also occurring in copolymers but in a reduced scale as the copolymer units hinder the unzipping of the complete chain [5]. Lufl et al, (2006) specify through mass spectrometry that the main degradation product of POM is formaldehyde [6]. Investigations on POM performed by pyrolysis or gas chromatography or mass spectrometry could identify upto 54 compounds formed during thermal degradation. But the major product which accounts for over 93% of the total degraded material is formaldehyde [7].

In 1880s, it was reported that formaldehyde could be quantitatively converted to hydrogen (H₂) in aqueous solutions under high basic condition and at room temperature [8]. Recently, Kapoor et al (1995), and Ashby et al (1993), proved that formaldehyde and water produced one hydrogen atom in H₂ formation. In addition, compared with other expensive hydrogen sources such as sodium borohydride and hydrazine hydrate, formaldehyde can be considered as an alternative hydrogen source because of its comparatively lower cost during large scale of production [9 & 10].

Shipley Fry et al,(1931) stated that aqueous solution of formaldehyde and sodium hydroxide yielded a very small amount of hydrogen. When cuprous oxide was added to the reaction mixture, it was reduced to metallic copper, which apparently catalyzed reaction, liberating pure hydrogen. This reaction may be represented by the following equation [11].

$$\text{HCHO} + \text{NaOH} \rightarrow \text{HCOONa} + \text{H}_2 \uparrow$$

Yingpu Bi et al (2008) reported that some nano-metal particles can catalyze hydrogen generation from formaldehyde solution [12]. The metal nanoparticles such as copper (Cu), gold (Au), platinum (Pt), and nickel (Ni) can significantly accelerate the hydrogen production rate at room temperature and atmospheric pressure. Among those catalysts, the copper nanoparticle was found to be the most active catalyst for hydrogen production [13].

Based on the above findings in literature survey, POM pellets were taken with nano metal copper catalyst and used in the production of hydrogen.
3. Experiment

Reaction mixture was prepared with 10 mg of copper nanomaterial (commercially purchased from Sigma Aldrich), 1M NaOH and 0.5 M HCHO (100 ml) in a flask and heated to boil. Hydrogen gas and sodium formate were expected to be produced [12].

3.1. Sodium Formate Assay under Direct Titration Method

Sodium formate assay was done with perchloric acid to calculate the percentage of presence of sodium formate in the reaction mixture. 5.0 ml of the reaction solution which contains 0.2 gms of sodium formate was dissolved in 50 ml of glacial acetic acid. The reaction mixture was gently heated and then cooled. Sodium formate with glacial acetic acid was titrated against 0.1 N perchloric acid using 0.1 ml Crystal violet indicator. Titration was stopped when the colour change occurred from violet to emerald green [14&15]. Blank determination was performed out for necessary correction.

\[ 1\text{N perchloric acid is equivalent to 68.01 gm of sodium formate.} \]
\[ \text{Each ml of 0.1N Perchloric acid is equivalent to 0.0068 gm of sodium formate} \]
\[ \% \text{ Sodium formate} = \frac{\text{ml} \times N \times 0.0068 \times 100}{\text{Weight of the Sodium formate}} \]
\[ \text{ml – Burette reading in ml} \]
\[ N - \text{Normality of Perchloric acid} \]

The weight of the sodium formate in the reaction mixture was calculated from the weight of sodium hydroxide taken in the reaction mixture. A random value 0.2gm of sodium formate, was taken and assessed in analytical method validation along with burette reading to know the percentage of sodium formate produced. As cited in the background study, when there is a reaction between formaldehyde and sodium hydroxide with cuprous oxide catalyst, equal amounts of sodium formate and hydrogen are produced. The idea behind this study is to measure the percentage of sodium formate, in order to know the percentage of hydrogen produced.

3.2. Analytical Method Validation

According to William Navidi (2008), Precision (the measuring process), Correlation coefficient and regression analysis were done with the data obtained through direct titration assay method [16].

3.2.1. Assessing Precision

Precision refers to the degree to which repeated measurements of the same quantity tend to agree with each other. If the repeated measurements come out nearly the same, the precision is high. If they are widely spread out, the precision is low.

The precision was experimented by analyzing five different preparations of sodium formate (Table 2). The standard deviation is a statistical measure of the precision for a series of repetitive measurements.

3.2.1.1. Relative Standard Deviation (Coefficient of Variation)

In probability theory and statistics, the relative standard deviation (RSD or %RSD) is the absolute value of the coefficient of variation. Coefficient of variation is a measure that is used to compare the dispersion in two series. Coefficient of variation is the percentage ratio of the standard deviation to the mean greater the coefficient of variation lesser will be the consistent. Also greater the coefficient of variation, greater will be the variability. The consistency increases with the decrease in the coefficient of variation.

3.2.2. Correlation Coefficient

Correlation may be defined as a statistical study of relationship between two or more variables. It helps to correlate the different weights of sodium formate (X) and the burette readings(Y) obtained during
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the titrations, with each weight of sodium formate. The measure of correlation is called the correlation co-efficient.

3.2.3. Regression Analysis
The regression analysis is highly useful to find out the relationship between one variable and one or more other variables. In this experiment different concentrations of sodium formate and burette reading obtained each time are recorded and analyzed for regression. The regression line equation helps to estimate the value of dependent variable, when the values of independent variables are used in the equation.

Regression line equation was drawn using the statistical software Minitab 15. This equation helps to predict the Y value that will be obtained next time the process is run with a specific concentration X (table.3).

3.2.3.1. Assessing Linearity
To find out the method of linearity, five different concentration of reaction mixture containing 0.04gms, 0.08gms, 0.12gms, 0.16gms and 0.2gms were taken and titrated against 0.1 N Perchloric acid. This test was performed to check the linearity (Table 2).

4. Results and Discussion
4.1. Results
As stated above, an assay to quantify the sodium formate in the reaction mixture was done. Using this value the amount of hydrogen produced was determined.

4.1.1. Sodium Formate Assay
The assay is calculated using the formula given in section 3.1.

\[ 2.958\% = \frac{8.7 \times 0.1 \times 0.68}{0.2} \]

Therefore the sodium formate present is 2.958%

4.1.2. Analytical Validation
4.1.2.1. Precision
In this experiment, the titration was repeated for five times with 0.2gms of sodium formate (Table.2) and the assay was very close from 2.941% to 2.975%. Hence high precision is found.

4.1.2.2. % Relative Standard Deviation
According to table 1 and 2, the lesser value of RSD is with 0.2gms of sodium formate than in table 2. It indicates that table 1 has minor inconsistency than table 2. It provides a good precision for taking 0.2gms of sodium formate for the experiment.

4.1.2.3. Correlation Coefficient
For our data, Correlation coefficient is 0.99997

It is more than 0.9 and it shows very high degree of correlation. This correlation suggests that the two data sets have a strong positive correlation. It shows that there is a strong positive correlation between the weight of Sodium formate (g) and the Burette Reading (ml) obtained.

4.1.2.4. Regression Analysis
Using MINITAB 15, regression equation is obtained (Table 3).

The equation is Burette Reading (ml) = 43.5 (Wt. Sodium formate (g)) + 0.0100

This equation can be used for calculating
Here the regression is a straight line (Fig.1). Hence the regression is a linear regression.

Figure 1:

**Linearity for Sodium Formate formation**

![](image)

<table>
<thead>
<tr>
<th>Wt. Sodium formate (g)</th>
<th>Burette Reading (ml)</th>
<th>Normality of Perchloric acid</th>
<th>% Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>8.7</td>
<td>0.1</td>
<td>2.958</td>
</tr>
<tr>
<td>0.2</td>
<td>8.75</td>
<td>0.1</td>
<td>2.975</td>
</tr>
<tr>
<td>0.2</td>
<td>8.7</td>
<td>0.1</td>
<td>2.958</td>
</tr>
<tr>
<td>0.2</td>
<td>8.7</td>
<td>0.1</td>
<td>2.958</td>
</tr>
<tr>
<td>0.2</td>
<td>8.65</td>
<td>0.1</td>
<td>2.941</td>
</tr>
</tbody>
</table>

Mean: 2.958
Standard deviation: 0.0120
% RSD: 0.406

The assay was in the range of 2.941% to 2.975%.

Table 2: Linear regression

<table>
<thead>
<tr>
<th>Wt. Sodium formate (g)</th>
<th>Burette Reading (ml)</th>
<th>Normality of Perchloric acid</th>
<th>% Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>1.73</td>
<td>0.1</td>
<td>2.941</td>
</tr>
<tr>
<td>0.08</td>
<td>3.5</td>
<td>0.1</td>
<td>2.975</td>
</tr>
<tr>
<td>0.12</td>
<td>5.25</td>
<td>0.1</td>
<td>2.975</td>
</tr>
<tr>
<td>0.16</td>
<td>6.94</td>
<td>0.1</td>
<td>2.949</td>
</tr>
<tr>
<td>0.2</td>
<td>8.7</td>
<td>0.1</td>
<td>2.958</td>
</tr>
</tbody>
</table>

Mean: 2.9597
Standard deviation: 0.0152
% RSD: 0.514

To find out the method of linearity as a graphical representation (Fig.1), Weight of the sodium formate was taken in X axis and burette reading was taken in Y axis.

Table 3: Regression Equation

Regression line equation was drawn using the statistical software **Minitab 15**

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Predictor Coef</th>
<th>SE Coef</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>0.01000</td>
<td>0.02482</td>
<td>0.40</td>
<td>0.714</td>
</tr>
<tr>
<td>Wt. Sodium formate(g)</td>
<td>43.4500</td>
<td>0.1871</td>
<td>232.25</td>
<td>0.000</td>
</tr>
</tbody>
</table>

SE Coef = The standard deviations (SE = Standard Error)
T = t value
P = p value
The Slope (b) was drawn as 43.5 and using minitab 15.
Intercept (a) = 0.0100
Regression equation $Y = bX + a$
$Y = 43.5 \times X + 0.0100$
Where $X$ = Wt. Sodium formate (g) and $Y$ = burette reading (ml)
Regression equation is
Burette Reading (ml) = 43.5 (Wt. Sodium formate (g)) + 0.0100

4.2. Discussions
Depolymerization of POM occurs at 100°C as per V.M. Archodoulaki et al, (2004) [17]. As water boils at 100°C, monomer units of formaldehyde are produced. Since formaldehyde gas is readily soluble in water, formalin is produced. According to Fry et al and Yingpu Bi et al, formaldehyde and NaOH produces hydrogen gas and equal amount of sodium formate [11,12].

The assay result for the presence of sodium formate confirms the production of Hydrogen and the assay helps to calculate the amount of hydrogen produced.

The titration value was thoroughly analyzed by employing statistical methods.
Precision value, Correlation coefficient and regression analysis were calculated by taking sodium formate concentration, burette reading as X and Y values respectively. These results suggest the high precision, high degree of correlation and linear regression for the above said data. According to Fry et al, for one molecule of sodium formate, one molecule of hydrogen is produced. Since equal amount of sodium formate and hydrogen are produced, percentage of sodium formate will be equal to that of hydrogen. In our experiment we got 2.958% of hydrogen production with POM scrape. Yingpu Bi et al showed almost 29% same experimental conditions with free formaldehyde.

5. Conclusion
Optimization experiments are being done by us to obtain more hydrogen. Also further research is in progress to measure the hydrogen production directly with Gas Chromatography (GC). Hence we conclude that formaldehyde can be considered as an alternative hydrogen source than high cost sodium borohydride and hydrazine hydrate. Here hydrogen was produced from POM waste plastics at no cost.

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References


