EFFECT OF DIFFERENT HEATING RATE ON THE THERMAL DECOMPOSITION OF VANILLIN IN AN OPEN REACTION VESSEL

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ABSTRACT

A study was done of the thermal decomposition of vanillin at different heating rate by thermogravimetric analyzer (TGA). The temperature and enthalpy of fusion of vanillin were calculated based on joint results of the DSC and TG experiments carried out using different heating rates varying from 3 to 20^0C/min. Thus it was made possible to compare the contributions to the total thermal effect of vanillin fusion and thermal decomposition process.

KEYWORDS

Thermogravimetric analysis (TGA), heating rate, differential thermal analysis (DTA), DSC, DTG

INTRODUCTION

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is majorly used in food, flavour and fragrance industries.[1] It also acts as an intermediate in the pharmaceutical industry. The production of ethylvanillin which is not present in nature and has to be produced synthetically is often carried out by the use of vanillin. Previous studies indicated vanillin was a main product in pyrolysis of lignin and vanillin contains several representative functional groups found in lignin structure, such as methyl, hydroxyl and formyl groups.[2] Vanillin chemistry is, thus, of interest to understand lignin's potential role as a feedstock for biomass-based aromatics. Among the parameters used in the pyrolysis of vanillin or biomass, the heating rate is one of the most important. The objective of the present work was to assess the influence of different heating rates on the pyrolysis of vanillin.

In the literature,[1,2] only a very few experimental studies and theoretical studies are available on vanillin pyrolysis to the best of author knowledge. Schin et al.[3] carried out experimental study on vanillin pyrolysis to study the reaction pathway leading to the formation of high value lower fraction aromatic compounds. Therefore, in order to better understand the pathways of vanillin pyrolysis and increase the conversion of product selectivity in the thermal decomposition of vanillin have been investigated at different heating rates namely 3 to 20^0C/min

MATERIALS AND METHODS

Commercial vanillin obtained from Fischer Scientific of analytical grade (95%). It was recrystallized from ethanol. This was the highest-grade purity available.

Thermogravimetric analysis of vanillin and measurements of mass losses (and the first derivative) versus temperature (TGA and DTG), measurements of heat flow versus temperature (DSC), measurements of temperature difference versus temperature (DTA) were determined using a SDT Q600 thermogravimetric analyzer under N_2(g) (purge). The experiments were performed in 25-300^0C temperature range, heating rates varying from 3 to 20^0C/min, typically 4-6 mg of sample was placed on a silica pan. Points of rapidly changing mass, slowly changing mass or where phase changes are known to occur (melting points etc.) were identified from the TGA, DTA, DSC and DTG plots.

RESULTS AND DISCUSSION

Results show that depending on the heating rate, different behaviours in the thermograms are observed. This is due to the different reactions taking place in the vessel induced by the different conditions under which the pyrolysis of vanillin is performed.

The TG experiments proved that vanillin decomposes slightly before melting. (Fig.1) We analyzed the heating rate influence on the melting point and mass loss after melting point. It has been found that at a faster rate, melting point was higher while the mass loss was smaller. (Table) The melting point variation can be

explained by cryoscopic effect. The resultant product of the decomposition acts as an impurity and decreases the melting temperature. Hence greater the mass loss, smaller be the melting point.

The results of DSC plot could be used directly to estimate heat of fusion. Increasing heating rate leads to an increase of heat of fusion. The values are given in Table. From the DSC plot it also appears that on increasing the heating rate, temperature range where liquid vanillin may exist also increases. It may be explained on the basis that at a high heating rate, heat is dissipated less easily and hence has a higher heat effect.

In each case only one major stage of mass loss is observed. (Fig.I) The pyrolysis reaction of vanillin in an open reaction vessel can be divided into two major reaction regions. These regions are dominated by different chemical processes associated with the mass loss stages observed in the TGA.

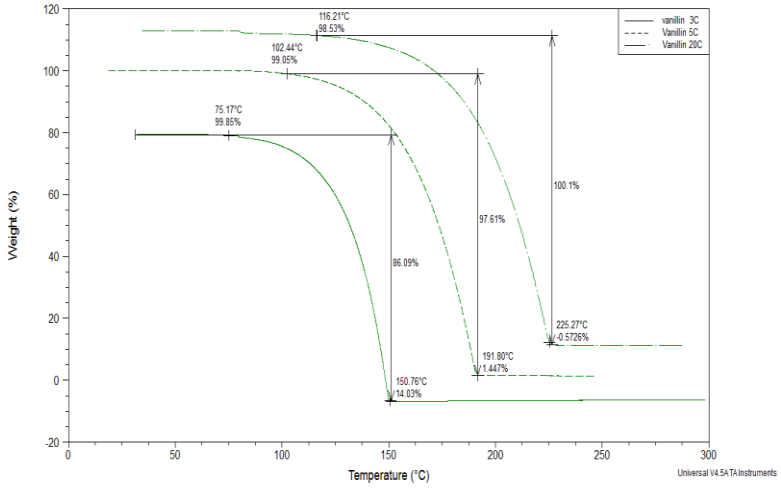

Fig.1. TGA study of vanillin pyrolysis using different heating rates

Shin et al.[3] carried out experimental study on vanillin pyrolysis to study the reaction pathway leading to the formation of lower fraction aromatic compounds. Schin et al[3] reported various products in the pyrolysis of vanillin under three sets namely primary (vanillin ionization fragments), secondary (guaiacol and catechol) and tertiary (phenol, benzene, CO) components. We found that when it was heated at a faster rate, the temperature at the start of the first decomposition and the final temperature on completion of first decomposition were higher than that obtained at a slower rate of heating. Furthermore, the difference between these two temperatures was also higher for faster rate.

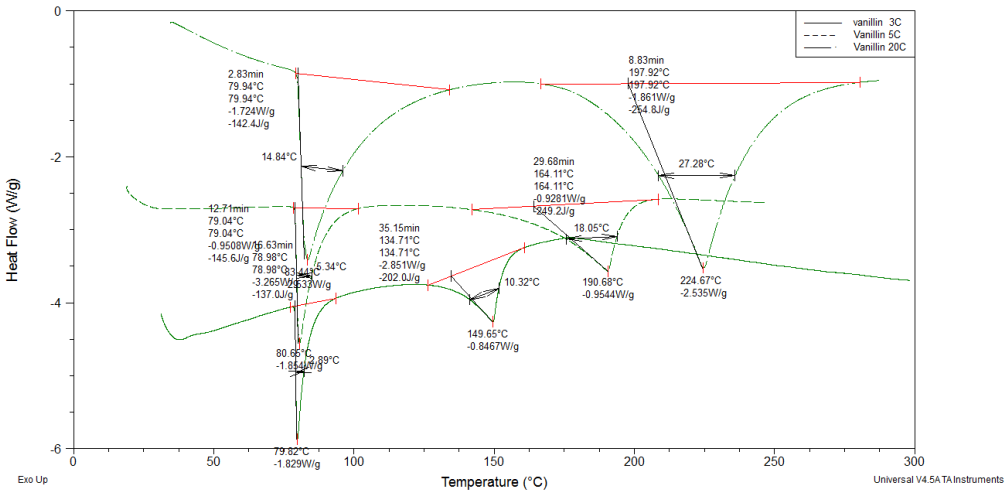

Fig2. DSC study of vanillin pyrolysis using different heating rates

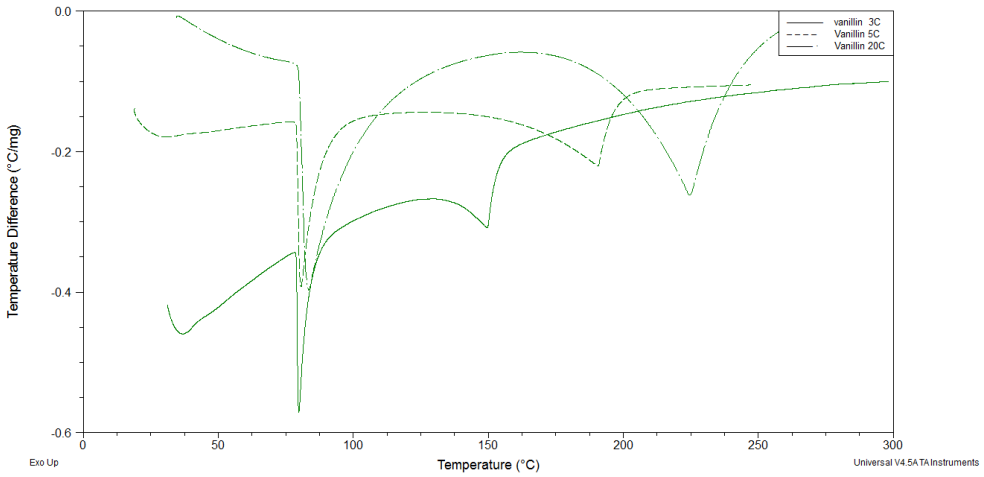

Fig.3. DTA study of vanillin pyrolysis using different heating rates

Changing heating rate leads to a simultaneous decrease of the effect temperature and an increase of the heat effect. If the heating rate increases, higher temperature is required to set off the decomposition process. At the same time, the amount of decomposition products decreases, which explains the difference between the effect temperature and heat effect. Fig. I-III show that while heating rate steadily decreases with a reduction in effect temperature, the heat effect rises. We observed decreasing mass loss with increasing scanning rate. A graph was plotted between melting temperature and heat of fusion versus heating rate.

The first endothermal minima respond to the fusion of vanillin, which in all three cases takes place at slightly different temperature range and the reaction heats absorbed are also slightly differ to each other. The second endothermic peaks correspond to the decomposition of vanillin into lower fraction aromatic compounds are much more varied, at a temperature range of 150-300^{0}C. They are undoubtedly related to the decomposition process as could be proved by DSC plot.

Table

Heating Rate (β)	Temperature range where liquid vanillin exists(^{0}C)	Heat of fusion (KJ/mol)	Melting temperature (^{0}C)
5^{0}C/min	2.89	137.0	78.98
10^{0}C/min	5.34	142.4	79.94
15^{0}C/min	9.89	145.6	80.65

References:-

1. Adesanya, S. A. and Wora A. Phytochemistry of plants used in traditional medicines. Oxford Science, New York, **1995**.
2. Kerler J., Verpoorte R. Vanilla Production: Technological, Chemical and Biosynthetic Aspects, FoodReviews International, **2001**, 17(2) 119-120.
3. Shin E., Nimlos, M. R. and Evans, R. J., A study of the mechanisms of vanillin pyrolysis by mass spectrometry and multivariate analysis, FUEL, **2001**, 80(12), 1689-1696.