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THE THERMOGRAVIMETRY AND PYROLYSIS OF DATE STONES

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ABSTRACT

The Al-Zahdi date stone as a source of energy and valuable chemicals is described. Thermogravimetry indicated that the material loses ca. 12% of its weight below 200 °C. The main decomposition reaction occurs above 205 °C and attains a maximum rate at 312 °C and resulted in the loss of ca. 50% of the initial weight. The decomposition is slightly affected by atmospheric oxygen especially at high temperatures (> 400 °C). The pyrolysis experiments were carried out in a pyrex reactor at 400 °C, where the sample was held on a sintered-glass disc and fluidized by an upward flow of N_2 gas. The gas, tar and solid yields of the pyrolysis were 41.5, 16.3 and 41.6%, respectively. The gaseous product was analysed and recommendations are given for the best use of the pyrolytic products.

INTRODUCTION

There is an increasing interest in the utilization and recovery of useful products from various waste materials of industrial, agricultural or domestic sources. Several international communities and industrial countries are funding large research and development projects in this area [1]. Pyrolytic routes are among the important conversion processes which are used to produce such useful products from waste materials [2–4].

Iraq is the largest producer of dates with more than 21 million date-palm trees and an annual production of about 400 thousand tons of the fruit. About 14% of the fruit is waste material in the form of stones (seeds). One of the most abundant kinds of dates in Iraq is the Al-Zahdi, which is used for fermentation industries and human food. The stones are now used in the production of animal feed.

The present work is an attempt to study the pyrolysis of the Al-Zahdi date stones with a view to finding some valuable materials within them.

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EXPERIMENTAL

Apparatus

A schematic diagram of the pyrolysis system is shown in Fig. 1. The system consists of a Pyrex tubular reactor (45 cm in length) with quick-fit ends and a disc of sintered glass placed at one third of the length. The reactor is fixed vertically within a 23-cm cylindrical electrical furnace so that the sintered-glass disc is 6 cm from the lower end of the furnace. The non-heated parts of the reactor were insulated thermally with the aid of few centimetres of asbestos fibres. A gas supply is applied to the lower part, while the upper part is connected to a laboratory-scale cyclone for solid separation. The gases leaving the cyclone pass through cooled traps and a condenser for liquid separation. Finally, the gases are taken for storage and chromatographic analysis.

Gas analysis was done on a Pye Unicam GC 204 gas chromatograph equipped with a spectra Physics Autolab minigrator. The working conditions and column-detector connections were as described previously [5].

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded simultaneously on a TA 500 Heraeus thermal analyser under static (air) atmosphere and flowing nitrogen. Samples weighing 4–5 mg were heated at a rate of 50 °C min^{-1} in platinum dishes from ambient temperature up to 450 °C.

The general composition of Al-Zahdi date stones was determined using standard methods of analysis and the results are given in Table 1. The physico-chemical characteristics of the date-stone oils are listed in Table 2.

Procedure

A sample of 2.0–3 g of date-stone powder was placed in the pyrex reactor which was then introduced into the vertical furnace. The furnace had been

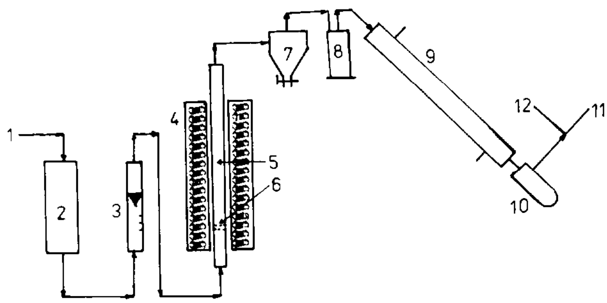

Fig. 1. Schematic diagram of the pyrolysis system. 1, Inert gas inlet; 2, dryer; 3, flow meter; 4 electric furnace; 5, pyrex-glass reactor; 6, sintered-glass disc; 7, cyclone; 8, trap; 9, condenser; 10, distillate collector; 11, to gas chromatograph; 12, to storage.

TABLE 1

The general composition of Al-Zahdi date stones

Component	%
Moisture	4.5
Ash	1.1
Protein	6.5
Fibre	20.5
Crude fat	8.0
Total sugar	6.5
Reducing sugars	2.4
Non-reducing sugars	3.5
Pectin	0.4

TABLE 2

The physical and chemical characteristics of Al-Zahdi date-stone oil

Parameter	
Oil (%)	8.1
Refractive index, 20 °C	1.4401
Specific gravity	0.9146
Saponification value	238
Iodine value	61.2
Acid value	1.2

previously heated to 400 °C and the flow rate of the purge gas, nitrogen, was adjusted to 500 ml min^{-1}. The experimental set-up was made such that the fitting of the reactor to other parts is to within 10–15 s. Preliminary runs indicated that the pyrolysis becomes appreciable 40–50 s after the introduction of the reactor into the furnace.

RESULTS AND DISCUSSION

Thermogravimetric analysis

The TG and DTG curves of Al-Zahdi date stones are shown in Fig. 2. The degradation under nitrogen reflects the complex nature of the material as it loses moisture and other low-boiling-point components at temperatures below 200 °C. The total weight loss recorded at this stage was 11.7%. A slow degradative volatilization occurs above 205 °C until 250 °C where the rate of the decomposition (DTG) increases significantly to attain a maximum at 312 °C. This main decomposition step involved a further 50% weight loss, which can be ascribed to the volatilization and degradation of oils, proteins,

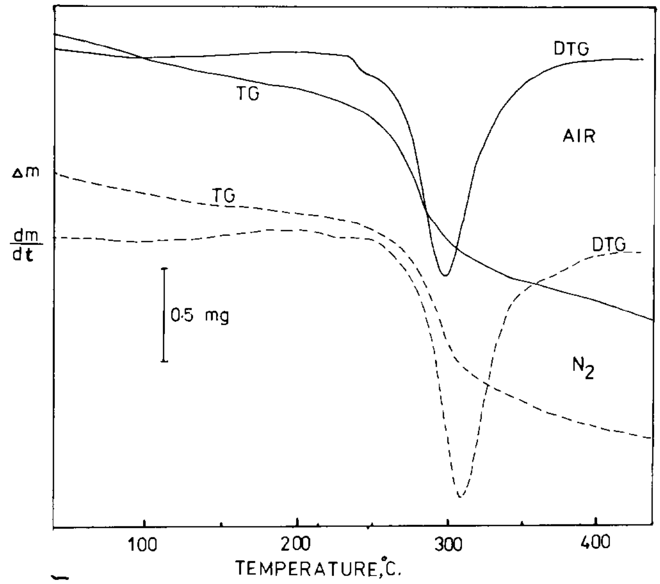

Fig. 2. TG and DTG curves of date stones under air and nitrogen atmospheres.

sugars and the backbone cellulose matter [6]. Above 400 ° C, the decomposition process proceeded slowly and ended with the char, which is the final product of most cellulose materials [3].

Under the oxidative atmosphere of air, the main features of the TG and DTG curves were retained, whilst the characteristic temperature tended towards lower values (Fig. 2). The decomposition process above 400 ° C was rather faster than that observed under N_2 atmosphere because of the (expected) oxidation (combustion of the residual material).

From the TG curves, the pyrolysis temperature was optimized at 400 ° C, which ensures that the main degradation reaction has occurred.

Pyrolysis: GC studies

The pyrolysis of the date-stone powder took place 40–60 s after the reactor was placed inside the furnace. This time interval was necessary for the particles to heat up to the decomposition temperature (ca. 250 ° C). White vapours were noticed to move up with the stream of the purge gas. Some of these vapours condensed in the cyclone which also removes the solid particulates from the gases. The main components of the cyclone liquids are oils, sugar-like compounds [7] and other minor high-boiling liquids [8]. Other condensable liquids, mainly water, are separated by the condenser and collected prior to the collection of the gaseous product.

In addition to char, tar and gas yields, another parameter, the percentage of (C + H) of the gaseous product, was considered. This parameter is often

TABLE 3

The pyrolysis products of date stones

Parameter	%
Char	41.6
Tar	16.3
Gas	41.5
C_{gas}	36.2
H_{gas}	2.3

TABLE 4

The chemical composition of the gaseous product of date-stone pyrolysis at 400 ° C

Component	%
Methane	3.2
Ethylene	0.9
Ethane	0.8
Propane	1.1
Methanol	14.3
Acetaldehyde	4.2
Carbon dioxide	42.5
Carbon monoxide	32.7

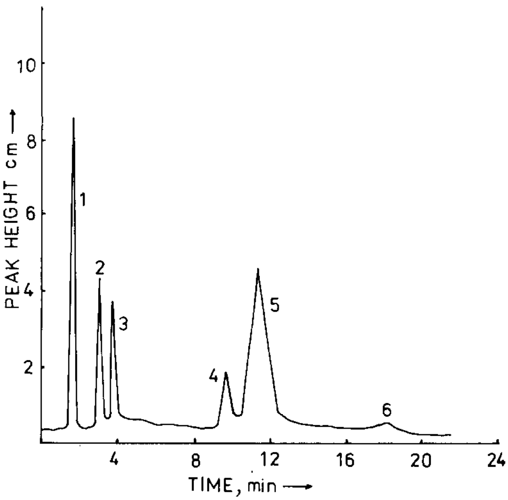

Fig. 3. Gas chromatogram of the gaseous products of date-stone pyrolysis at 400 ° C. 1, Methane; 2, ethylene, 3, ethane; 4, propane; 5, methanol; 6, acetaldehyde.

used to characterize the pyrolysis products in terms of energy content [9,10], %C + %H on the basis of the GC analysis and the molecular mass of each component (Table 3).

A typical chromatogram of the gases is shown in Fig. 3. The quantitative evaluation of the chromatogram is given in Table 4. It is clear that the major components of the gas were carbon oxides and methanol. The latter compound is important industrially and as a starting material in organic synthesis. Thus, the pyrolysis experiments could be directed to improve the yield of methanol by modifying the working conditions and the use of catalysts.

CONCLUSION

Thermal processes offer an effective means for the recovery or conversion of the energy contents of date stones and other lignocellulose materials [2–5]. The volatile organic matter of the date stones can be recovered as a gas and a tar on pyrolysis. In the future, the use of wood pyrolysis for the production of vinegar and methanol may encourage the application of this technique for extracting such a valuable product from date stones, which gives a relatively higher yield of methanol (Table 4). The other gaseous components may be separated and employed to supply the heat for pyrolysis. Furthermore, the pyrolysis tars are not desirable liquid-fuel precursors and are probably best consumed on site to meet process-energy requirements [11]. In addition, the pyrolysis process could be extended so that the primary volatile products pass over catalyst beds such as metals, metal oxides or their mixtures, and gasification principles could be used which benefit from the reaction of hydrogen with carbon monoxide, produced in situ, to improve the yield of the desired product, methanol [12].

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