

GEPOLYMERS AND SYNTHETIC POLYMERS; A COMPARATIVE STUDY OF THE  
ISOTHERMAL PYROLYSIS KINETIC BEHAVIOR.

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ABSTRACT

The isothermal pyrolysis kinetic behavior of fossil fuels (oil-shales, coals) and synthetic polymers was studied under similar experimental conditions. The kinetic behavior of the synthetic polymers (vinyl polymers, nylons and cross-linked styrene with divinylbenzene polymers) followed rather closely the well known depolymerization models published in the literature. However the kinetic behavior of the geo-polymers was rather different. A kinetic model which can explain this difference is offered. It attributes the different kinetic behavior of the synthetic and the geo-polymers to their different structural features.

INTRODUCTION

Several processes designed for liquefaction-gasification of solid fossil fuels (oil shales & coals) are characterized by rapid heating of the sample, followed by essentially isothermal retorting with the subsequent rapid removal of the pyrolysis products. It was pointed out by several workers [1-9] that the rate of organic pyroproducts formation under such conditions can be described by a linear combination of several first order reactions. However, the chemical meaning of this discrepancy is not yet understood. Recently we have pointed out [10] that the kinetic behavior of common synthetic polymers is rather different, and cannot be described by linear combination of first order reactions. We have also reported [10] the discovery of a unique oil shale sample, whose kinetic behavior was different from that of the common fossil fuels previously studied [1-9] and resembled the kinetic behavior of the synthetic polymers. This discovery indicates a connection between the kinetic behavior of geo-and synthetic polymers. The thermal depolymerization of synthetic polymers is better understood than that of the geo-polymers. The main objective of the present paper is to use the well known

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depolymerization models available in the literature for synthetic polymers in order to achieve a better understanding of the kinetic behavior of geo-polymers.

## EXPERIMENTAL

The experimental methodology and instrumentation were previously described [4,9].

## RESULTS AND DISCUSSION

Fig. 1 shows two curves of volatile organic pyroproducts formation-rate versus time obtained from the isothermal pyrolysis of two common fossil fuels (oil shale and coal). The same overall behavior was observed for other samples (see Fig. 2 in Ref.[9]). These profiles are characterized by an immediate maximum of the reaction rate and a decrease with the progress of the reaction. It was pointed out by us [4,9] and by other workers [1-3,5-8] that this behavior can be described by a linear combination of several parallel independent first order reactions.

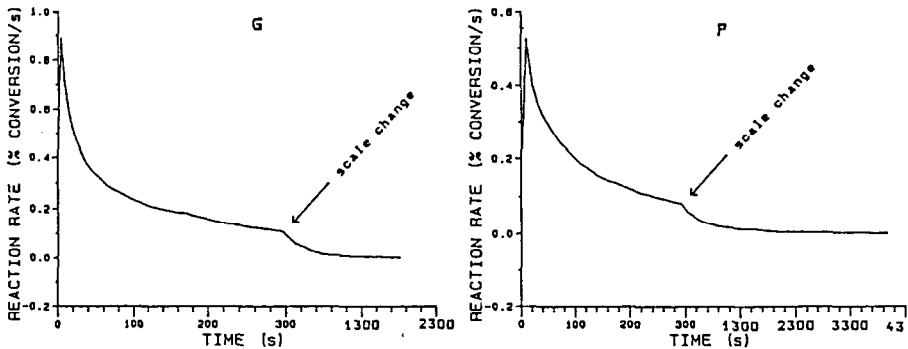


Fig. 1: Isothermal pyrolysis of two common fossil fuels (450°C)  
 G=Green River Red Point mine oil shale (U.S.A.),  
 P=Secretary Pretoria Waterderg coal (S.A.).

Fig. 2 shows a curve of reaction rate versus time obtained by pyrolysis of poly(propylene). We have observed the same overall behavior for many other synthetic polymers [poly(ethylene-glycol), nylons, poly(ethylene), cross-linked styrene with divinylbenzene polymers, etc.].

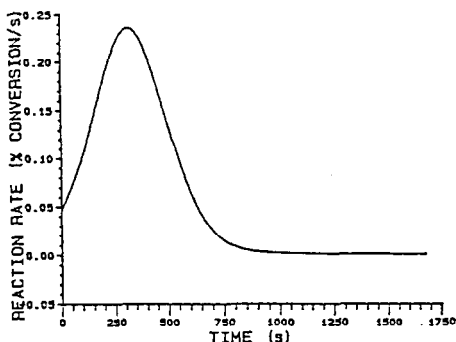


Fig. 2:  
Isothermal pyrolysis  
of poly(propylene) (450°C).

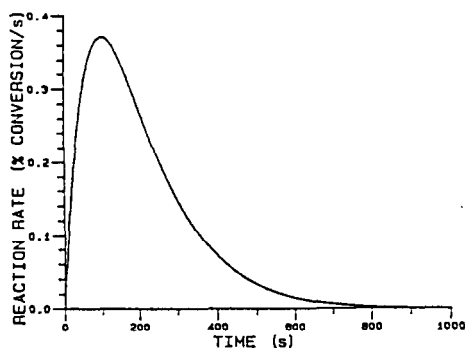
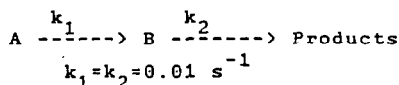
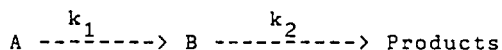


Fig. 3:  
Computer simulation of  
the sequence:



The thermal depolymerization of "simple" (chain) synthetic polymers is better understood as compared with that of the geo-polymers (fossil fuels). Two main models are known: 1) "unzipping" (to give the monomer) typical for 1,1 disubstituted vinyl-polymers (this mechanism is quite unique and we did not find any parallel process in the present study). 2) random depolymerization [11]. The random depolymerization model assumes cleavage of the polymeric chain by random bond rupture, which can yield either shorter chains that stay in the system or smaller fragments (if the cleavage is near a chain end), which volatilize and leave the system. Therefore, the rate of volatile pyrolyzate formation depends on the number of chain ends rather than on the quantity of the polymer. The precise mathematical formulation of the random depolymerization model [11] is quite complicated and difficult to follow. We have found that drawing a parallel between this model and a simple sequential reaction is a useful way to make the random depolymerization kinetic behavior perceptible:



Where A - analogous to the number of polymeric bonds, B - analogous to number of chain ends, P - volatile products

If we assume a situation in which  $k_1 = k_2$ , based on the idea

that the same bond cleavage yields either chain ends or volatile products, then computer simulation will yield Fig. 3. At the beginning of the reaction the number of chain ends is negligible, hence at  $t=0$  the reaction rate  $dP/dt=0$  whereas, with the progress of the reaction the number of ends increases, therefore accelerating the formation of volatiles which are measured as products;  $dP/dt$  increases until it reaches a maximum, then more ends are volatilized than formed leading to a decrease in  $dP/dt$ . It is obvious that the general shape of this profile resembles that of Fig. 2.

In our recent publication [10] we have reported the discovery of a unique oil shale sample whose kinetic behaviour was different from that of the common fossil fuels (Fig. 1) and resembled the random depolymerization behavior (Fig. 3). The kerogen of this oil shale (Hartley Vale Torbanite, Australia) has an homogeneous structure in comparison with the heterogeneous structure of common fossil fuels. This kerogen originated from the known Botryococcus braunii algae. The outer walls of this algae contain large amounts of biopolymer which is built of long chain hydrocarbons [12] The kerogens produced by this algae have a very high H/C atomic ratio and a low content of hetero atoms. NMR, IR, and Pyrolysis-GC data indicate the predominance of  $CH_2$  groups [12] The kinetic behaviour of the Hartley Vale oil shale led us to believe that 1) there is a linkage between the kinetic behaviour of common fossil fuels and the random depolymerization model, and 2) homogeneity and heterogeneity are key terms in understanding the difference between the kinetic behaviour of synthetic and geo-polymers.

The lower part of Fig. 4 shows three possible routes in which a volatile fragment (P) can be generated from a large molecule such as synthetic or geo-polymer. (A) the volatile fragment can be generated by a single bond rupture (peripheral groups). (B) the volatile fragment can be generated by a cleavage of two or more chemical bonds of the same strength. (C) the volatile fragment is generated by the cleavage of two or more chemical bonds of different strengths (the chemical bonds are marked by small anchors of different sizes). The upper part of Fig. 4 reveals the expected shape of the generation rate versus time curves.

It is quite obvious that the generation rate of type (A) fragments will follow a first order reaction, since the generation rate is proportional to the momentary amount of such fragments which did not volatilize (this could be pictured as shaking a tree

of its fruit, at the beginning of such a process, the rate of fruit falling will be the fastest and it will slow down as the quantity of fruit, still on the tree, decreases). Furthermore, if we assume that we have type (A) fragments which are bonded to their environment by chemical bonds of different strengths, then the measured generation rate of such fragments will follow linear combination of first order reactions (the ripe fruit contribute the fast "reactions" and the unripe fruit the slow "reactions").

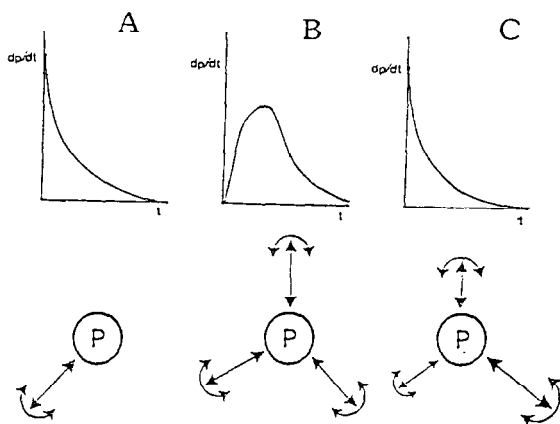
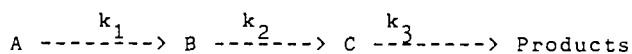


Figure 4: (see text)

The generation of the (B) type fragments, is analogous to the generation of volatile fragment from the inside of a long polymer chain e.g. one has to cleave two bonds in order to have a volatile fragment, or in the case of a crossed-linked polymer one has to cleave more than two chemical bonds in order to generate a volatile fragment. This situation is analogous to a sequential reaction:



when: A= a fragment attached to its environment by three chemical bonds.

B= a fragment attached to its environment by two chemical bonds.

C= the fragment is attached to its environment by one chemical bond.

If we assume  $k_1=k_2=k_3$ , then the  $dP/dt$  versus time curve will

resemble the one in Fig. 3 (this statement was verified by a computer simulation).

The (C) type fragments were generated by more than one bond rupture as the (B) type fragments. However in this case  $k_1 \neq k_2 \neq k_3$  hence the slowest reaction will be the rate determining step (RDS) and will dominate the kinetics. Thus the generation rate of the (C) type fragments will follow a first order reaction kinetics similarly to the (A) type fragments. Therefore if we have a population of such fragments in which the RDS bond of each one of them is of different type then the generation rate of these fragments will follow linear combination of first order reactions!.

We would like to emphasize that making analogy between the random depolymerization model and a simple sequential reaction is a severe oversimplification of the real situation. Jellinek [11] has derived a detailed theory for polymer degradation and has formulated rate equations for many of the important reactions: random chain scission, initiation, chain-end initiation, depropagation, transfer, first- and second order termination, and disproportionation. From these rate equations, he derived expressions for volatile rate formation. Application of this theory is outside the scope of the present paper.

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