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Catalytic hydrothermal conversion of polypropylene

Fatima Abubakar, Ibrahim Alfayez, Habib Suleymanov, James McGregor *

University of Sheffield, Department of Chemical and Biological Engineering, Mappin Street, Sheffield S1 3JD, UK

A R T I C L E I N F O

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A B S T R A C T

This work reports preliminary-stage studies demonstrating the highly selective conversion of polypropylene to short-chained olefins *via* hydrothermal catalytic processing. The production of such monomer species from waste polymers is highly desirable and has the potential to play a key role in plastics recycling and in the circular economy more broadly. Addition polymers such as polypropylene are, however, known to be particularly challenging to recycle into propene or other short-chained alkenes. Herein, we have compared and contrasted acid- and base-catalysed hydrothermal processing at a temperature of 360 °C, analysing the products of reaction by gas chromatography – mass spectrometry (GC-MS) and Fourier transform infrared (FTIR) spectroscopy. Employing the basic catalyst K_2CO_3, results in a 95 % yield of gas-phase products of which 52 % are propene and 9 % butenes on a mole basis. The solid acid catalyst HZSM-5 also selectively yields gaseous products, 21 % of which are propene and 22 % are butenes, the reaction proceeding via β-scission of the starting oligomers. These results represent a potential step-change in the production of monomer units from addition polymers, highlighting the potential value of catalytic hydrothermal processing in the field of polymer recycling.

1. Introduction

Plastics are ubiquitous in modern life to the extent that they have been suggested as the potential key geological makers of the Anthropocene, identifying the present era as the 'plastic age' [1]. Global plastic production doubled in the first 20 years of this century, reaching 460 Mt in 2019, with only 9 % of this being recycled after losses are accounted for [2]. The development of effective and efficient recycling routes for plastics and polymers is therefore an issue of paramount importance. The present work is an initial proof-of-concept investigation, highlighting a potential step-change in the use of hydrothermal processing for the recovery of monomers and other valuable species from plastics, employing polypropylene as an exemplar feedstock.

Physical recycling and pyrolysis represent the most widely researched avenues for polymer recycling [3–5]; for instance, Valanciene *et al.* have studied the zeolite catalysed pyrolysis of polypropylene [6]. Both of these approaches however have limitations. Physical recycling results in products with inferior physical properties to the original material [7], while pyrolysis requires high energy inputs and harsh reaction conditions [8]. Hydrothermal processing represents a promising alternative for the recycling of waste polymers, including polypropylene [9,10]. Hydrothermal processing describes a thermochemical conversion technology, which operates at relatively low temperatures (180–360 °C) and at sufficient pressure (<50 bar) such that the water which comprises the reaction medium remains in the liquid phase. Depending on reaction conditions the products may be solid (carbonisation), liquid (liquefaction) or gaseous (gasification) [11–15].

Previous studies have shown that polypropylene is particularly recalcitrant to conversion under hydrothermal conditions, with, *e.g.*, long processing times required even to achieve relatively low conversions [10,16]. Herein, we aim to demonstrate the successful conversion of polypropylene to propene and other monomer species, *e.g.* butene, through the use of two different catalysts: K_2CO_3 and HZSM-5. The former catalyst is an alkaline material that has previously been successfully employed in the hydrothermal processing of biomass, while the latter is an acidic catalyst that has been employed, *e.g.*, in the cracking of waste plastics [5,10,17,18]. This therefore allows a comparison of both acidic and basic catalysts which have shown efficacy in reactions and processes closely related to those discussed herein.

2. Experimental

2.1. Materials

For the purposes of this study and in order to investigate the

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* Corresponding author.
E-mail address: james.mcgregor@sheffield.ac.uk (J. McGregor).

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mechanism of reaction without interference from, *e.g.* unknown impurities, pristine polypropylene (isotactic, average Mw ~250,000, average Mn ~67,000, particle size 2.4 mm ± 0.2 mm) (Sigma-Aldrich, 99.5 %) was used to simulate waste polymer. K_2CO_3 (Sigma-Aldrich, $\geq$ 99 %), and HZSM-5 (SiO_2:Al_2O_3 ratio 38:1, surface area $\geq$250 m^2g^{-1}, pore volume $\geq$0.25 ml g^{-1}; 30 wt% binder (pseudo-boehmite)) (ACS Material, Pasadena, USA) were employed as catalysts and used without further modification. Other materials used were compressed helium (BOC, 99.99 %) and distilled water.

2.2. Reaction studies

The catalytic hydrothermal liquefaction of polypropylene was conducted in a 100 ml EZE-Seal reactor constructed from Hastelloy-C (Parker Autoclave Engineers) described previously [19,20]. The reactor was charged with polymer and water in the ratio 1:10, *i.e.* 2 g polymer: 20 g water. The catalyst was introduced at either 10 wt% in the case of H-ZSM-5, or 0.9 M in the case of K_2CO_3. Prior to reaction the system was purged four times with He. The reactor was then heated at 6 °C min^{-1} to the desired reaction temperature of 360 °C. Upon reaching this temperature the impeller was initiated at 500 rpm and the reaction then proceeded for a period of 2 h. The total reaction time will, in reality, exceed 2 h as some conversion will take place during the initial heating period. After this time, the reactor was cooled to room temperature by immersing it in water ice. Gaseous products were vented *via* a valve to 1 l sample bag. The solid and liquid products were then removed from the catalyst and the reactor was rinsed twice with 10 ml dichloromethane in order to dissolve any remaining soluble components; this solution was then added to the removed sample. The liquid and solid phases present were then separated by filtration for subsequent analysis, with the solid product being dried overnight in an oven.

2.3. Product analysis

The reaction has the potential to produce liquid- (either aqueous-soluble or insoluble), gaseous- and solid-phase products. Suitable analytical techniques were therefore selected in order to characterise the species formed in each phase; these are described in Sections 2.3.1 – 2.3.3.

2.3.1. Liquid-phase products

Gas chromatography – mass spectrometry (GC-MS) (Shimadzu QP2010SE) was employed to analyse the liquid samples collected. A DB-5MS column of length 25 m and internal diameter 0.23 mm was used. The temperature was ramped from 30 – 60 °C at 6 °C min^{-1}, and then to 300 °C at a rate of 5 °C min^{-1} before being held at this temperature for 10 min. Quantification was conducted through the generation of calibration curves using solutions of known concentration of analyte. The yield of liquid-phase reaction products was calculated as a percentage on a mass-basis as:

$$\%Yield = \frac{C_{prod} \times V_t}{m_{poly}} \times 100$$

where C_{prod} is the concentration of the product determined after reaction, V_t is the total volume of liquid and $m_{0,\mathrm{poly}}$ is the initial mass of polymer added to the reactor.

2.3.2. Gas-phase products

The formation of gas-phase species was quantified through comparing the increase in pressure at the end of reaction to the increase in pressure when no reactants or catalyst were present. The collected gas samples were manually injected in the GC-MS (Shimadzu QP2010SE) equipped with a Rt-Q-Bond plot column (length 30 m, internal diameter 0.32 mm). The temperature programme entailed ramping the temperature from 40 – 250 °C at 15 °C min^{-1} and then holding at this final temperature for 5 min.

2.3.3. Solid-phase products

Fourier transform-infrared (FTIR) spectrometry performed on a Shimadzu IR Affinity-1S equipped with a Specac attenuated total reflectance (ATR) accessory. Spectra were acquired over a 4000–400 cm^{-1} range, averaged over 16 scans and with a resolution of 4 cm^{-1}. Additionally, the stability of the stability of the zeolite catalyst under hydrothermal conditions was evaluated by X-ray diffraction (XRD) as detailed in the Supplementary Information.

3. Results and discussion

Two different catalysts have been compared and contrasted to determine their efficacy in the hydrothermal reduction of polypropylene. The results of reaction in the presence of the alkaline solution-phase catalyst K_2CO_3 are presented in Section 3.1, while those employing the acidic solid-phase catalyst HZSM-5 are presented in Section 3.2.

3.1. K_2CO_3 catalyst

The use of K_2CO_3 as a catalyst resulted in the highly selective production of gas-phase products, in particular propene - the constituent monomer. In addition, a small quantity of liquid-phase products were produced. After reaction no solid-phase products were identified, indicating the complete conversion of polypropylene had occurred. This compares to a conversion of only 12 % in the absence of a catalyst. This latter value is a similar conversion to that achieved previously by dos Passos *et al.* who obtained ~15 % conversion, predominately to liquid-phase products, in a 20 ml reaction vessel operating in a heating profile designed to mimic continuous HTL processes [16]. Two distinct liquid phases were present: an oil-like organic phase and a water-rich aqueous phase, alongside the gaseous products.

Gas-phase products comprised 95 % of the material produced from the hydrothermal processing of polypropylene, as determined through observing the pressure increase after reaction as compared to the pressure increase in the absence of reactants (30 bar at 633 K) and determining the total number of moles of gas present via the ideal gas law. The high yield of gaseous species is attributed to the use of K_2CO_3 as a catalyst, which has previously been associated with high gasification activity in the hydrothermal processing of biomass [21–23]. Previous studies of the hydrothermal conversion of polypropylene at higher temperature (400–500 °C) and longer reaction times (4–6 h), but in the absence of a catalyst, resulted in gas yields of only 20–28 % [24]. dos Passos and co-workers investigated the KOH-catalysed hydrothermal conversion of polypropylene [16]. In contrast to the results presented herein where K_2CO_3 was employed as the catalyst, that work showed no identifiable change in the structure in the polymer, with >90 % of the solid remaining after reaction, while formation of liquid- and gas-phase products was retarded when compared to the reaction in the absence of a catalyst. This stark difference, despite the variations in operating conditions between the two studies, suggests that K_2CO_3 is a superior catalyst for polypropylene conversion than KOH. The efficacy of K_2CO_3 may arise from its conversion to potassium bicarbonate, $KHCO_3$, in the presence of water. The formed $KHCO_3$ then acts as a secondary catalyst in hydrothermal processing [25,26].

The major component of the gas-phase produced was the constituent monomer of the polymer substrate, *i.e.* propene. Propene comprises 52 % of the gas-phase on a mole basis. Other species observed were 2-butenes (9 %), pentane (8 %) and carbon dioxide (31 %). The selective production of the monomer is highly desirable but also highly challenging; typically, addition polymers such polypropylene do not undergo depolymerisation and hence other approaches such as (catalytic) thermal cracking are employed to recycle them [27,28]. Catalytic hydrothermal processing may therefore represent a promising avenue for future exploration in the selective depolymerisation of polyolefins including polypropylene. The CO_2 observed in the gas-phase is likely to be produced through the water-gas-shift reaction *via* a formate intermediate [18,29]. This reaction will also yield H_2, which acts as an additional reducing agent in the conversion of the hydrocarbonaceous material [30,31].

Considering the liquid products detected, only trace amounts of organic material are observed in the aqueous phase. This indicates that liquid-phase products exist preferentially in the organic phase. Table 1 shows the range of hydrocarbons identified in the organic-phase and the chromatogram peak area. Olefins, cyclic species, linear paraffins and alcohols are all observed in the range C_8-C_{20}. Previous studies employing K_2CO_3 as a catalyst and supercritical water as the reaction medium, rather than subcritical water as employed herein, have also shown the formation of branched olefins and cyclic hydrocarbons in this carbon number range [24]. The product distribution in the present work is dominated by two species: 2,4-dimethyl-1-heptene (28.3 mole% of the organic-phase) and 1-pentyl-2-propyl cyclopentane (23.4 mole% of the organic phase). The mechanism of formation of 2,4-dimethyl-1-heptene is well established in the thermal pyrolysis of propylene [32,33]. It is proposed that the same mechanism operates here in the hydrothermal conversion of the polyolefin. Specifically, reaction occurs through the scission of carbon-carbon bonds at position 1 and 3, and the cleavage of C-H bonds at position 4, as shown in Fig. 1. One key difference between pyrolysis and hydrothermal processing is however that the former is typically less selective, producing a broader range of products [34]. Notably, no 2-methyl-1-pentene is observed in the present work; this is commonly reported as a product of the thermal degradation of polypropylene and is typically formed *via* a similar mechanism to 2,4-dimethyl-1-heptene but with carbon-carbon bond scission resulting in a C_6 species as opposed to a C_9 species [35,36]. The lack of 2-methyl-1-pentene is attributed to the fact that the reaction medium in the present study is high-temperature water. Conducting the same study in a hydrocarbon solvent (toluene) for comparison did yield significant quantities of the C_6 species, albeit that 2,4-dimethyl-1-heptene remained the major product [37]. The reason for the inhibition of one pathway under hydrothermal requires further investigation.

3.2. HZSM-5 catalysts

Employing HZSM-5 as the catalyst in the hydrothermal conversion of polypropylene yielded gas-phase products and a solid residue. No products were detected in the liquid-phase by GC-MS, while FTIR spectroscopy indicated only the presence of water, *i.e.* the reaction medium. This indicates an exceptional selectivity of this catalyst to produce a very narrow distribution of hydrocarbonaceous products. A comparison of the yield to different phases of material for the H-ZSM-5 and K_2CO_3 catalysed reactions is presented in Table 2.

Table 1
Products observed in the hydrothermal conversion of polypropylene at 360°C for 2 h after heating at 6°C min^{-1}, employing K_2CO_3 as the catalyst. The polymer to water ratio 1:10. Species comprising <1 % of the organic liquid-phase are excluded.

Compound	Mole fraction in (organic) liquid-phase
4,4,5-Trimethyl-2-hexene	1.5
2,4-Dimethyl-1-heptene	28.3
1,3,5-Trimethylcyclohexane	4.1
2,2-Dimethyl-3-octene	1.7
2,5-Dimethyl-1,6-octadiene	1.2
4-Methyldecane	2.2
1,2-Diethyl-3-methylcyclohexane	1.7
2,3,6,7-Tetramethyloctane	1.9
7-Methyl-1-undecene	2.5
1-Isopropyl-1,4,5-trimethylcyclohexane	1.6
1-Pentyl-2-propyl cyclopentane	23.4
11-Methyldodecanol	7.8
3-Hexadecene	9.7
3-Octadecene	1.8
2-Hexyl-1-dodecanol	6.0
3-Eicosene	1.5

GC-MS analysis of the gas-phase products obtained from the hydrothermal conversion of polypropylene with HZSM-5 were butene (22 %), propene (21 %) and CO_2 (57 %), with an overall yield of 80 % to gas-phase species. In contrast no gas-phase species were formed in the control reaction in the absence of a catalyst, consistent with previous studies of catalyst-free polymer hydrothermal liquefaction [38,39]. The alkenes produced in the presence of HZSM-5 are formed *via* the pathway described in Fig. 1, analogous the process employing K_2CO_3 as the catalyst (Section 3.1), albeit that propene was the dominant product produced over the basic catalyst. Previous studies on the catalytic pyrolysis of polypropylene have also reported that the use of ZSM-5 increases selectivity to C3-C5 hydrocarbons [40], with more acidic catalysts favouring gaseous products [41]. An advantage of the hydrothermal reaction medium utilised in the present work is the enhanced selectivity and narrower product distribution than that observed from pyrolysis. The CO_2 detected is, again analogous to when K_2CO_3 is used, produced *via* the water gas shift reaction, also yielding hydrogen which acts as a reductant in the process. Although similar products are produced over both catalysts, as is commonly observed when comparing the action of acidic and basic catalysts in hydrothermal processing [42], notable difference are observed. A significant difference between the gas-phase reaction products observed with HZSM-5 and those produced using K_2CO_3 is that no cyclic species or alkanes are observed for the solid acid catalyst. This is ascribed to HSM-5 catalysing β-scission of the oligomers forming light alkenes. Solid acid catalysts possessing Brønsted acidity, such as HSZM-5, are well-established to preferentially crack alkene oligomers to smaller alkene units through reaction at those Brønsted sites [43,44]. It is therefore proposed that a similar reaction network operates during hydrothermal processing of polypropylene over HSZM-5.

FTIR spectroscopy analysis of the solid residue present after reaction showed that the signal was dominated by the framework stretching vibrations of HZSM-5 (Fig. 2). A small quantity of hydrocarbonaceous material is evidenced by the presence of C-H stretching vibrations in the region 2750–3000 cm^{-1}. This may be coke on the surface of the zeolite or unreacted polypropylene. The carbonyl stretch at 1750 cm^{-1} indicates that some oxygen has been incorporated into the hydrocarbon product. While framework stretches associated with HZSM-5 are identified by FTIR spectroscopy, a comparison of the X-ray diffractograms of the fresh catalyst and that after exposure to the hydrothermal processing environment reveal a significant loss of crystalline structure. This suggests that while the solid acid catalyst is highly active for this reaction future research endeavours should be directed towards identifying materials with similar catalytic properties but with greater stability under these reaction conditions.

4. Conclusions

In this preliminary work the base (K_2CO_3) and acid (HZSM-5) conversion of polypropylene under hydrothermal conditions has been investigated. Both catalysts yield gaseous products with high selectivity, with K_2CO_3 preferentially producing the monomer propene (52 % of gas-phase products), with smaller quantities of butenes (9 %). Employing HZSM-5, 21 % of the gaseous products are propene and 22 % are butenes, with the majority of the gas-phase being made of CO_2 (57 %). The ability to selectively produce light alkenes from the starting polymer is of particular value, and hence this work demonstrates the potential role of hydrothermal catalytic processing of waste polymers in the future circular economy.

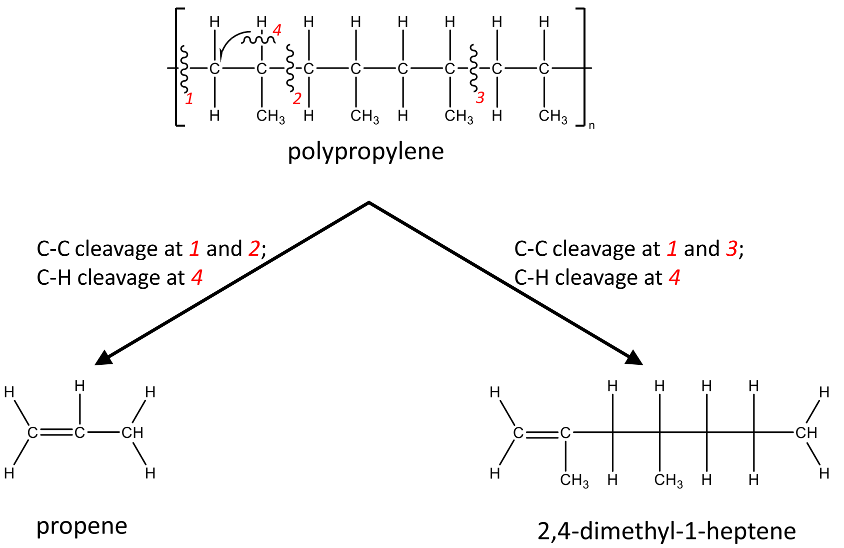

Fig. 1. Schematic representation of the mechanism of hydrothermal polypropylene conversion, adapted from Supriyanto [32]. Wavy curves indicate the bonds which may undergo scission during reaction.

Table 2
Distribution of products between the gas, liquid and solid phases for the hydrothermal conversion of polypropylene catalysed by K_2CO_3 and H-ZSM-5. Reaction conditions: 360°C for 2 h after heating at 6°C min^{-1}; polymer to water ratio 1:10.

Compound	K_2CO_3	H-ZSM-5
Solid-phase	0 %	20 %
Liquid-phase	5 %	0 %
Gas-phase	95 %	80 %

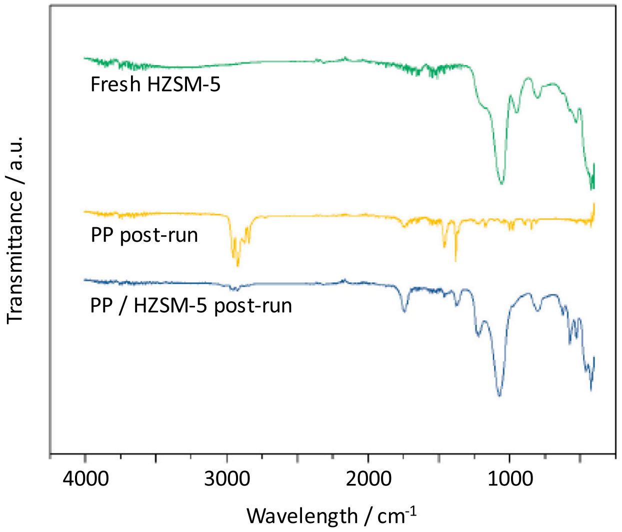

Fig. 2. FTIR spectra of fresh HSM-5 (top, green), and the solid residue arising from the hydrothermal conversion of polypropylene (PP) in the absence (middle, yellow) and presence (bottom, blue) of HZSM-5 as a catalyst.

CRediT authorship contribution statement

Ibrahim Alfayez: Conceptualization, Formal analysis, Investigation. **Habib Suleymanov:** Investigation. **James McGregor:** Writing – review & editing, Supervision, Data curation, Conceptualization. **Fatima Abubakar:** Writing – original draft, Investigation, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Fatima Muhammad reports financial support was provided by Petroleum Technology Development Fund. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2024.114807.

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