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Oligomerisation of Alkenes by Radical Initiation

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Abstract:

The use of di-*tert*-butyl peroxide (DTBP) as initiator for the radical oligomerisation of 1-octene and pentene, typical Fischer−Tropsch-derived products, was studied in the temperature range 100−200 °C. Using this approach, the favourable product distribution of radical oligomerisation (viz. less branched products in contrast with the catalytic oligomerisation of alkenes) can be obtained, whilst operating at less severe conditions than normally required for the radical oligomerisation reaction in thermal oligomerisation. The less branched products find application as plasticizer and detergent alcohols, poly(α-olefin) (PAO) lubricants, and high-cetane distillate. Dimerisation and trimerisation of the alkenes were observed in the temperature range 100−200 °C at 10−20 bar pressure, which coincides with the activation temperature range of the di-*tert*-butyl peroxide. Although technically feasible, the use of an initiator to lower the operating temperature of thermal oligomerisation could not be justified economically.

Introduction

In previous work, thermal oligomerisation of Fischer−Tropsch (FT)-derived alkenes was shown to be effective in providing a diesel product with acceptable cetane number and an oil product with acceptable viscosity index.[1] The relative simplicity of the thermal process enabled it to be preferred over the catalytic process using BF_3 as catalyst. Unfortunately, severe reaction conditions had to be employed (i.e., temperatures of 335−385 °C, pressures of 50−180 bar, and residence times of 0.8−3.0 h).

The use of radical initiators for polymerisation of alkenes has been well established for many years.[2−4] Thermal treatment does not cause chain branching of alkenes,[5] resulting in a product that is less branched than that of the BF_3-catalysed process. Products with a low degree of branching could provide desirable properties for applications such as plasticiser[6] and detergent alcohols,[7] synthetic poly-(α-olefin) (PAO) oils,[8] and high-cetane diesel fuel.[9]

We consider that the addition of a radical initiator could decrease the severity of the operating conditions required for thermal oligomerisation. In this study we present our initial results using pentene and octene as feedstocks with di-*tert*-butyl peroxide (DTBP) as radical initiator.

Experimental Section

The oligomerisation reaction was carried out in an autoclave (1-L 316 SS Parr pressure reactor). The temperature and pressure were adjusted as required (see Supporting Information, Table S3, for full details), and a stirring speed of 720 rpm was used to ensure effective mass transfer. Where appropriate, oxygen was replaced by removing the air under vacuum followed by the addition of argon gas to the reactor. This procedure was repeated three times to ensure maximal removal of oxygen. In a typical experiment, alkene (300 mL; 2.8 mol pentene or 1.9 mol octene) was stirred at 720 rpm and heated. At the desired temperature, DTBP (10 mL; 0.05 mol) was added, and a sample was taken at the time indicated.

Analyses. Product quantification was carried out using an HP 5980 gas chromatograph equipped with an FID, on a PONA column (dimensions 50 m × 0.2 mm × 0.5 μm) at 180 kPa pressure, with 0.2 μL sample and a split ratio of 1:100. After an initial hold time of 10 min the temperature was increased from 35 to 290 °C at a heating rate of 4 °C/min with a final hold time of 30 min.

Results and Discussion

Baseline Experiment. A baseline experiment with octene as feed was performed without adding initiator (DTBP). The results are given in Table 1 (experiments 1, 2). The results in Table 1 indicate that no oligomerisation took place at short contact times (1 h) in the absence of an initiator. At longer contact times (16 h), some oligomers were observed but were negligible in comparison with the results observed in the presence of initiator, being over 2−3 orders of magnitude lower. The contribution of nonradical initiator-induced reactions could therefore be neglected under these reaction conditions and in the time scale of the experiments.

Evaluation of the Inertness of the Reactor. It is known that metal surfaces have varying influences on hydrocarbon reactions. Some metals may promote radical reactions (e.g., autooxidation),[10] whereas others decrease the rate of the reaction.[11] The possible effect of the metal on carbon

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Table 1. **Initial experiments with 1-octene and pentene, at a temperature of 150 °C and a pressure of 10 bar**

expt #	temp (°C)	reaction time (h)	initiator (mol)	feed (mol)	benzene[g] (mol)	products[d] (%)
1	150	1	0.00	1.0	1.68	0.0
2	150	16	0.00	1.0	1.68	0.1
3	150	1	0.05	1.9[c]		7.1
4	150	1	0.05	1.9[c]		8.7
5[e]	150	1	0.05	1.9[c]		7.5
6[a]	150	3	0.05[b]	1.9		0.0
7[a]	150	16	0.05[b]	1.9		4.8
8	150	1	0.05[b]	1.9		10.4
9	150	16	0.05[b]	1.9		12.1
10[f]	150	1	0.08[b]	1.9		2.5
11	150	1	0.08[b]	1.9		2.9
12	150	1	0.05	1.0	1.68	2.0
13	150	64	0.05	1.0	1.68	4.0

[a] In the presence of air. All other experiments were conducted in an argon (99.999%, Fedgas) atmosphere. [b] DTBP (98%, Sigma-Aldrich). All other experiments were conducted with DTBP (91%, Polifin, now Sasol Polymers). More detailed analyses of the DTBP are given in the Supporting Information (Table S1). [c] Experiments 3−5 were conducted with pentene (Sasol Synfuels, Secunda) as feed. All other experiments were conducted with 1-octene (98%, Sigma-Aldrich, by analysis 99.3%) as feed. The feed compositions, as analysed by GC, are listed in Table 1 (octene) and Table 2 (pentene). A more detailed composition of the pentene is given in the Supporting Information (Table S2). [d] All material heavier than the feed was considered product. Only the liquid products were analysed by GC. [e] Experiment was conducted with a glass liner in the autoclave. [f] Ethanol added. [g] Benzene (99%, NT Laboratory Supplies)

formation previously noted[11−13] was not considered a threat because the operating temperature was much lower and such effects were not seen with stainless steel during thermal oligomerisation.[1] The potential effect of carrying out radical oligomerisation in a metal autoclave was investigated by performing some reactions with a glass lining using pentene as feed. The results are reported in Table 1 (experiments 3−5). It is clear that the results obtained with and without a glass liner were similar. All subsequent reactions were, therefore, carried out without a glass liner present in the autoclave.

Effect of Oxygen. The effect of oxygen was studied using octene as feed, and the results are presented in Table 1. More oligomerisation products were obtained in the absence of air (Table 1, experiments 8 and 9) than in the presence of air (experiments 6 and 7). Increasing the reaction time from 3 h (experiment 6) to 16 h (experiment 7) resulted, as expected, in an increase in oligomerisation products but still less than that obtained in the absence of air at a reaction time of 1 h. Subsequent experiments were, therefore, carried out in the absence of air, since the presence of air can lead to the formation of partial oxidation products,[14,15] resulting in unwanted side products.

Effect of Ethanol Addition (Determination of the Extent of Termination of Reaction). The addition of ethanol to determine the extent of the termination of the reaction was investigated using octene as feed. The possibility that the radical reactions were not terminated by cooling the samples following reaction was evaluated, and the results are reported in Table 1 (experiments 10, 11). The oligomers obtained were similar when an excess ethanol was added to terminate the reaction, indicating that no further reaction took place after the sample had been drawn from the reactor. Hence, for subsequent experiments, no ethanol or other reaction-terminating agents were added to samples taken.

Table 2. **GC analysis of pentene feed and product in mass %**

component	pentene (feed)	pentene (product)[a]
C_4 compounds	1.6	0.0
3-methyl-1-butene	0.5	0.0
acetone	0.6	0.1
isopentane	3.2	0.7
1-pentene	5.3	1.5
2-methyl-1-butene	2.6	0.8
pentane	12.7	6.1
trans-2-pentene	45.6	23.4
2-methyl-2-propanol + *cis*-2-pentene	16.4	18.2
2-methyl-2-butene	10.2	6.3
2-methyl-propanal	0.2	0.1
1-propanol	0.1	0.2
C_5 naphtenes	0.8	0.6
C_6 compounds	0.3	1.2
methylethyl ketone (MEK)	0.1	0.1
2-pentanone	0.0	0.1
C_7 compounds	0.0	0.1
C_8 compounds	0.0	1.3
xylenes	0.0	0.6
C_{10}-dimers	0.0	34.2
$C_{10}H_{22}$	0.0	0.6
$C_{11}H_{24}$	0.0	0.0
undefined	0.0	3.8
total	100.0	100.0

[a] Experiment 19. Reaction conditions were 150 °C, reaction time 16 h, 10 mL of initiator, 10 bar pressure, and 300 mL (2.8 mol) of pentenes as feed, and air was removed from the reactor.

Effect of Addition of a Nonreactive Diluent (Benzene). The effect of the addition of a diluent was investigated with octene as feed. It is known that the use of a solvent has an effect on the half-life of peroxides. In nonpolar solvents, such as benzene, the DTBP half-life is longer than in polar solvents such as chlorobenzene. From the results in Table 1 it is clear that the addition of benzene (experiments 12, 13 compared with 8) decreases the amount of oligomers formed.

Oligomerisation Reactions of Pentene and Octene. Additional experiments using DTBP as initiator were then conducted at other temperatures (see Supporting Information, Table S3). Typical products resulting from the reaction of pentene are shown in Table 2 (experiment 19) and for octene in Table 3 (experiment 43) and discussed below.

Pentene. The pentene feed and product data in Table 2 show that C_{10} dimers made up 34.2 mass % of the product and compounds $>C_{10}$ made up 3.8 mass % of the product. Although the feed contained 1.6 mass % C_4 compounds (alkanes and alkenes) no C_4 compounds were reported in the product. The acetone content decreased from 0.6 to 0.1 mass %. The acetone in the product is much lower than in the product obtained from octene feed. This is probably because the pentene run was done at milder conditions (lower

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Table 3. **GC analysis of octene feed and product in mass %**

component	octene (feed)	octene (product)[a]
acetone	0.0	4.9
2-methyl-2-propanol	0.0	11.3
1-hexene	0.0	0.1
1,3-dimethylcyclopentane	0.0	0.0
di-*tert*-butyl peroxide	0.0	0.0
1-octene	99.3	53.6
4-octene	0.0	0.1
3-octene	0.1	0.6
octane	0.3	0.5
trans-2-octene	0.1	2.7
cis-2-octene	0.0	1.0
1-ethyl-2-methylcyclopentane	0.0	0.3
nonane	0.1	0.0
$C_{16}H_{32}$	0.0	0.5
$>C_{16}H_{32}$	0.0	22.4
1-decene < *x* < C16	0.0	1.8
total	100.0	100.0

[a] Experiment 43. Reaction conditions were 200 °C, reaction time 16 h, 45 mL of initiator, 20 bar pressure, and 300 mL (1.9 mol) octene as feed, and air was removed from the reactor.

temperature (150 vs 200 °C) and pressure (10 vs 20 bar) and with a smaller amount of initiator (10 mL for the pentene experiment vs 45 mL for the octene experiment) while having the same volume of feed, resulting in less decomposition product formed. The fraction reported as 2-methyl-2-propanol + *cis*-2-pentene is only slightly higher in the product, possibly due to the decrease in *cis*-2-pentene and less formation of 2-methyl-2-propanol due to the addition of a smaller volume of initiator compared to the case of the octene feed. The only aldehyde detected in the feed (2-methyl propanal), decreased from 0.17 to 0.05 mass %, while the only alcohol detected in the feed (1-propanol), increased from 0.07 to 0.21 mass %. The two ketones detected in the feed (MEK and 2-pentanone) increased from 0.06 to 0.13 and 0.00 to 0.08 mass %, respectively. MEK, being a minor product of decomposition of DTBP, indicates some decomposition of DTBP despite the relatively low acetone content in the product.

The *o*-xylene (0.17 mass %) and *m*,- *p*-xylenes (0.47 mass %) detected in the product by GC analysis probably originated from the wash solvent.

Octene. Limited octene double-bond isomerisation was observed. This could be due to premature termination of the octene radicals. Theoretically, at a temperature of 200 °C (as calculated by Gibbs-energy minimization with Aspen using the Redlich−Kwong−Soave equation of state), the ratio of 1-octene/3-octene/4-octene/*cis*-2-octene/*trans*-2-octene should be 1:19.2:9.3:3.2:14.7 at equilibrium.

Although no DTBP was detected in the GC analysis of feed or product (the injector temperature was higher than the decomposition temperature of DTBP*)*, one of the main decomposition products of DTBP, acetone (4.9 mass %) was detected in the product. An important by-product of initiation and minor product of DTBP composition, 2-methyl-2-propanol (11.3 mass %) was also detected in the product.

C_{16} alkenes (0.5 mass %) were formed, indicating dimerisation of the C_8 feed. In the product 22.4 mass % compounds $>C_{16}H_{32}$ were found, indicating oligomerisation. The presence of 1.78 mass % compounds between 1-decene and C_{16} (1-decene < *x* <C_{16}), with a carbon chain length longer than the feed material, also indicates oligomerisation.

The formation of C_8 cycloalkanes (1-ethyl-2-methylcyclopentane and 1,2-dimethyl-cyclohexane) can be explained as follows: Cyclisation only occurred when octene was used as reagent, the linear C_8 olefin being converted to C_5 and C_6 rings with substituents, and was not observed when pentene was used as feed. This phenomenon could be due to the radical attacking itself, which would also explain the lack thereof in the pentene.

$$R_6\text{-CH(OR)-C}^{\bullet}\text{H}_2 \xrightarrow{\text{radical rearrangement}}$$

$$\text{R-C}^{\bullet}\text{OR-CH}_3 \xrightarrow{\text{self-attack, minus }\bullet\text{OR}}$$

1,2-dimethylcyclohexane or 1,2-methylethylcyclopentane

This study has demonstrated that oligomerisation of pentene and octene for applications such as plasticiser and detergent alcohol precursors and poly(α-olefin) (PAO) lubricants can be technically feasible. Due to the fact that free radicals have a low tendency to isomerise, the oligomers formed via this process can be less branched than in the catalytic process. Experiments with pentene resulted in higher alkene conversion (and thus more oligomer product produced) per mole of decomposed DTBP than with octene. Without further optimisation studies, 38 mass % of product could be obtained from pentene at 150 °C and 10 bar, 16 h reaction time and 10 mL of initiator with a productivity of 20 mol C_5 feed consumed per mole DTBP decomposed. For both pentene and octene feedstocks it was found that there is a linear dependence between the amount of feed consumed (and thus oligomer products formed) and the initiator decomposition.

Conclusions

It was shown that the severe temperatures of thermal oligomerisation could be lowered by the addition of a radical initiator. Pentene and octene can thus be upgraded by radical oligomerisation to precursors for specific applications. The oligomerisation rates obtained in these unoptimised conditions were, however, not sufficient to make the process economically viable. A rough order of magnitude economic calculation, based on the best results obtained, indicated that the productivity of the initiator was an order of magnitude too low to generate a positive cash flow.

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Supporting Information Available

GC-FID analysis of the DTBP used (Table S1); more detailed GC-FID of the pentene feed and product (Table S2); a table of experimental conditions for the oligomerisation experiments (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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