

Impact of α -Olefins and Diolefins from Polyolefin Pyrolysis Oil on the Catalytic Cracking Mechanistic Pathways

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Highlights

- Catalytic pyrolysis of pyrolysis oil model compounds was studied.
- Cracking of olefins and diolefins displayed distinct product distributions through different reaction pathways.
- Diolefins in the pyrolysis oil intensify the aromatization and coke formation.

1. Introduction

The employment of chemical recycling for polyolefin waste management, a promising eco-friendly approach, has gained substantial attention across scientific and industrial sectors. The plastic pyrolysis oil can be blended with naphtha and other hydrocarbon feeds in steam cracking units to yield light olefins or undergo catalytic upgrading and cracking processes. Research has shown that pyrolysis oil derived from polyolefins typically consists of approximately 50-60% mono and diolefins, with cyclic hydrocarbons (naphthenes and aromatics) comprising around 10-15% and the remaining fraction mainly consists of paraffins[1]. The presence of paraffins does not pose significant challenges in the production of light olefins from pyrolysis oil. The primary hurdles for steam cracking units arise from the olefins and diolefins. Studies on these units have revealed that when the feed contains more than 2% olefins, secondary reactions intensify. It is important to note that pyrolysis oils contain various olefins, classifiable into α -olefins and iso-olefins. Based on earlier research [1, 2], pyrolysis oil from polypropylene, containing iso-olefins as byproducts, presents fewer challenges in the production of light olefins due to steric hindrance from methyl groups. The main challenges are associated with linear α -olefins and diolefins, the primary components in the thermal pyrolysis of polyethylene waste [3], which are why 1-decene (α -olefin) and 1,9-decadiene (diolefin) were selected as model compounds for plastic pyrolysis oil in this research. The objective is to discern differences in the cracking mechanisms of olefins and diolefins, with particular attention to secondary reactions such as aromatization and coke formation. This will provide insights into how mid-range carbon number (C_{10}) linear-olefins (1-olefins) and diolefins, which result from the chain scission of long-chain hydrocarbons, influence the overall polyolefin cracking process, ultimately affecting the production of light olefins, aromatics, and cyclic compounds.

2. Methods

Thermal and catalytic pyrolysis experiments were done in a fixed bed quartz reactor (D_{in} : 9 mm, D_{out} : 13 mm) coupled with an online GC-TCD. A preheater line at 250 °C vaporizes the liquid feed and N_2 as the carrier gas, facilitates a continuous feed flow to the fixed bed reactor. Molar composition of the feed (10% 1-decene or 1,9-decadiene & 90% N_2), N_2 flowrate (116.32 ml/min), liquid hydrocarbon flowrate (0.1 ml/min), amount of catalyst (14.5 mg, W/F_{HC} : 15.24×10^{-2} kg.s/mol), reactor pressure (1.3 bara), and catalyst bed height (catalysts mixed with a fixed amount of inert medium particles 125-150 μ m quartz, 0.9907 g) were kept constant. 1-decene (α -olefin) and 1,9-decadiene (diolefin), as model compounds, were purchased from Thermo Fisher scientific with purity of 96% and 97%, respectively. Using the steam-treated (at 800 °C for 4h) ZSM-5 catalyst (sample: CBV 5524G, $SiO_2/Al_2O_3 = 50$), cracking of olefins and diolefins were conducted at varied temperatures and contact times.

3. Results and discussion

During the catalytic pyrolysis of 1-decene, which occurred within the temperature range of 250 °C to 450 °C at varying contact times, the conversion process included isomerization followed by chain scission. This led to the production of lighter olefins. The dominant reaction pathway was skeletal isomerization, generating branched C₁₀ isomers (nonene with a methyl group), which was notably more prevalent than double bond rearrangement, particularly at higher conversion levels. As conversion increased, chain scission of 1-decene isomers intensified, resulting in the production of lighter olefins such as butene and propylene. Consequently, in the case of 1-decene catalytic pyrolysis, the initial reactions involved isomerization, followed by chain scission, ultimately leading to the production of light olefins. Later in the process, cyclization of olefins occurred (Figure 1-left). In contrast, during the catalytic pyrolysis of 1,9-decadiene (diolefin), the major products were cyclic compounds, particularly cyclohexenes with an alkyl group, and light olefins and diolefins. Elevating the reaction conditions, such as increasing temperature and contact time, resulted in greater conversion of 1,9-decadiene into cyclic compounds and chain scission into lighter diene compounds. Notably, the presence of lighter conjugated diolefins generated through chain scission of 1,9-decadiene, facilitated the Diels-Alder reaction, promoting cyclization, aromatic production, and, consequently, coke formation. This phenomenon was less prevalent during the cracking of 1-decene, as it did not produce conjugated diene compounds, thus limiting the cyclization process. Hence, the reaction pathways of 1,9-decadiene catalytic pyrolysis, as illustrated in Figure 1 (right), included chain scission, cyclization, ring expansion, and the formation of cyclohexene rings, which subsequently converted to aromatic compounds.

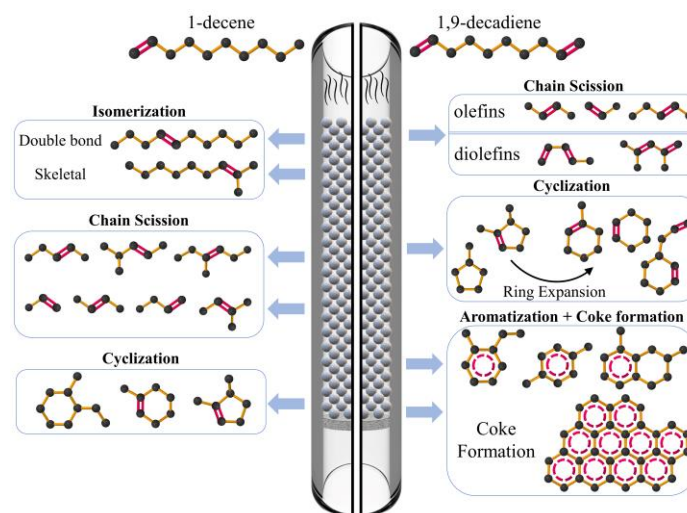


Figure 1. Overall product distribution and yields from catalytic pyrolysis of 1-decene and 1,9-decadiene using ZSM-5 catalyst at different temperatures

4. Conclusions

In conclusion, the analysis of structural characteristics olefins and diolefins indicates a significantly higher likelihood of forming butadiene derivatives within the diolefins category compared to α -olefins. Consequently, diolefins exhibit enhanced susceptibility to Diels-Alder reactions, leading to the eventual creation of diverse cyclic compounds, culminating in aromatics and polyaromatics. In light of these considerations, a comprehensive assessment, encompassing the proportion of polypropylene in the pyrolysis feedstock, alongside the quantification of linear diolefins and α -olefins, offers precise insight into the operational dynamics of the ensuing light olefin production unit.

References

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Keywords

Pyrolysis; ZSM-5; Reaction mechanism; Model compounds