

Production of lower alkenes and light fuels by gas phase oxidative cracking of heavy hydrocarbons

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Abstract

The gas phase oxidative cracking (GOC) and non-oxidative pyrolysis of heavy hydrocarbons were investigated, with decalin (decahydronaphthalene) and tetralin (tetrahydronaphthalene) as the model compounds for naphthenic hydrocarbon and aromatic hydrocarbon, respectively. Unlike pyrolysis, the ring rupture of decalin or tetralin molecule and the decoking ability of system were significantly enhanced due to the introduction of O₂ in GOC. For GOC of decalin, both the lower alkenes and the light fuels were obtained. At lower temperatures the light fuels mainly contained alkyl benzene, alkyl cyclohexane and isoparaffins, while it was rich in BTX (benzene, toluene and xylenes) at higher temperatures. A 38.9% yield of lower alkenes and 48.0% yield of light fuels (BTX mass content: 59.9%) at 100% decalin conversion were obtained under the conditions of 800 °C and decalin/O₂=0.5. For GOC of tetralin, both the dehydrogenation and the cracking reactions dominated the reaction routes, resulting in a high mass content of alkyl naphthalene and alkyl benzene in the light fuels. The estimation of O₂ distribution in the products demonstrated that O₂ participated primarily in the oxydehydrogenation reactions at low temperatures, while mainly in the partial oxidation reactions at high temperatures to produce CO_x (x=1, 2).

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1. Introduction

Lower alkenes are commercially produced by the pyrolysis of hydrocarbons in tubular reactor coils installed in externally fired heaters. Feedstock plays a vital role in the production cost of the lower alkenes. Although lower alkanes such as ethane and propane are much preferable for the production of lower alkenes, those heavy feedstocks, such as naphtha, diesel oil, crude oil and residual oil, are also to be widely used in some regions where there are abundant resources of heavy stuff [1]. The heavy feedstock generally consists of paraffins, isoparaffins, naphthenes and aromatics, the mass concentrations of which greatly depend on the producing areas. For example, naphthene content in virgin naphtha of Taching oilfield (China) is as high as 46 wt.% [2]. Those naphthenic and aromatic compositions, however, are not suitable for the pyrolysis process to produce lower alkenes, due to their high molecule stability and the tendency to agglomeration. Therefore, how to take

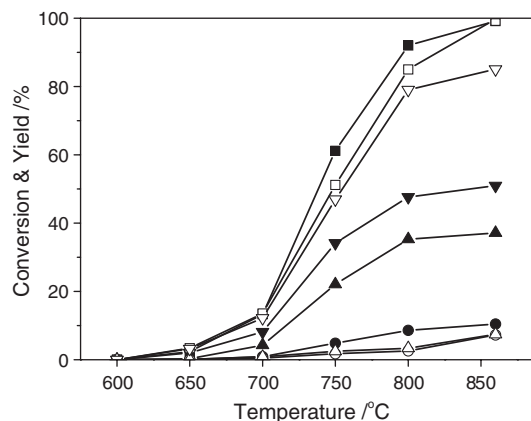


Fig. 1. Conversions and selectivities versus temperature for non-oxidative pyrolysis of decalin and tetralin with a nitrogen dilution ratio of 90% and feed flow rate of 100 ml/min (STP). Decalin: ■, conversion; ●, yield of lower alkenes; ▲, yield of lower alkenes; ▼, yield of light fuels. Tetralin: □, conversion; ○, yield of lower alkenes; △, yield of lower alkenes; ▽, yield of light fuels.

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Table 1
Light fuel yields and compositions for non-oxidative pyrolysis of decalin (90% nitrogen dilution ratio and 100 ml/min (STP) feed flow rate)

T (°C)	Fuel yield (%)	Fuel composition (wt.%)					
		Paraffins	Isoparaffins	Naphthenes	Alkylbenzenes (BTX ^a)	Olefins	Others
700	8.2	0.0	3.5	34.2	59.1 (9.0)	2.8	0.4
750	34.2	2.0	4.2	28.2	63.9 (33.7)	0.9	0.8
800	47.6	0.0	3.1	16.7	79.6 (41.6)	0.6	0.0
860	50.9	0.0	0.4	8.4	90.7 (66.3)	0.5	0.0

^a Benzene, toluene, xylenes.

Table 2
Light fuel yields and compositions for non-oxidative pyrolysis of tetralin (90% nitrogen dilution ratio and 100 ml/min (STP) feed flow rate)

T (°C)	Fuel yield (%)	Fuel composition (wt.%)						
		Paraffins	Isoparaffins	Naphthenes	Alkylbenzenes	Alkyl-naphthalenes	Olefins	Others
700	12.2	0.0	0.0	0.0	48.1	51.9	0.0	0.0
750	47.0	0.0	0.0	0.0	38.4	61.6	0.0	0.0
800	79.0	0.0	0.0	0.0	37.3	62.5	0.0	0.2
860	85.1	0.0	0.0	0.0	38.9	60.8	0.0	0.3

full advantage of those feedstocks (rich in naphthenes and aromatics) becomes a challenging topic for the production of lower alkenes from heavy stuff.

The gas phase oxidative dehydrogenation (ODH) of C_2 – C_4 alkanes [3–5] and gas phase oxidative cracking (GOC) of higher hydrocarbons [6,7] to lower alkenes have attracted much attention since the early 1990s. Burch et al. [3] found that some homogeneous conversion of ethane to ethylene occurred in the oxidative coupling of methane, and their successive work on ODH of ethane [8] and propane [9] showed that the homogeneous ODH reactions were competitive with the heterogeneous catalytic reactions over the best catalysts available at that time. Lemonidou and Stambouli [5] compared the pyrolysis and the catalytic and non-catalytic ODH of *n*-butane, and found that nearly 90% selectivity to lower alkenes with 22% conversion of butane can be achieved in non-catalytic ODH process, which was much higher than that either in the pyrolysis or in the catalytic route under comparable conditions. Most of the work in ODH of lower alkanes focused on the break of C–H bonds; however, the situation should be somewhat different when higher hydrocarbons are employed, because the cracking of C–C bonds in their molecules becomes more remarkable. The work of Liu et al. [10,11] on GOC of hexane and cyclohexane showed that much high cracking performances can be found at low temperatures. For example, at 750 °C the GOC conversion of hexane and lower alkene yield were 85% and 51%, respectively, which were significantly higher than those in the pyrolysis process: 29% and 21%. The similar reaction performance was also found in GOC of cyclohexane (87% conversion and 44% lower alkene yield at 750 °C), while its pyrolysis conversion and alkene yield were only 8% and 6%, respectively. It is evident that, when compared with pyrolysis process, GOC process exhibits much distinct advantage in the case of inferior feedstock such as cycloalkane.

In this paper, decalin (decahydronaphthalene) and tetralin (tetrahydronaphthalene) were employed as the model compounds for heavier naphthene and arene, and their GOC processes were investigated for lower alkene production. The ring rupture or ring

opening of these multi-ring compounds are much more relevant to the upgrading of fuel oils [12], for example, the ring rupture of decalin to *n*-decane will increase the cetane number of kerosene fractions, while its ring opening to alkyl benzene will improve the octane number of gasoline fractions. Therefore, GOC of decalin or tetralin to light fuels (gasoline and kerosene) were also studied in this paper.

2. Experimental

2.1. Experimental apparatus

The reactions were conducted in a straight tubular quartz reactor (6 mm inner diameter \times 300 mm) under atmospheric pressure. A chromel–alumel thermocouple inside a closed quartz thermowell (2 mm outer diameter \times 240 mm), which was located in the center of the reactor, was used to record the reaction temperatures freely along the reactor. The reactor was mounted in a programmable tubular furnace (120 mm long),

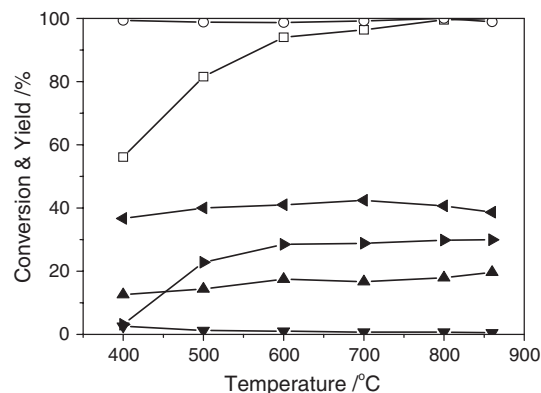


Fig. 2. Conversions and yields versus temperature for GOC of decalin with a decalin/ O_2 molar ratio of 0.5 and feed flow rate of 100 ml/min (STP). \square , Conversion of decalin; \circ , conversion of O_2 ; \blacktriangle , yield of CO ; \blacktriangledown , yield of CO_2 ; \blacktriangleright , yield of lower alkenes; \blacktriangleleft , yield of light fuels.

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