Efficiency improvement of pyrolysis

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Abstract

Ethylene production by pyrolysis of hydrocarbon gases (ethane, propane, butane) and liquid fractions provides better selectivity to ethylene at higher temperatures, as has been well documented in studies. Temperature increase accelerates chain-radical reactions of ethylene formation. Acceleration of chain-radical process can be achieved at a given temperature by the presence of an initiating agent of radical formation in the feedstock. Bimolecular reaction of allene (propadiene) with either alkane or alkene hydrocarbons and is an extremely rapid reaction of radicals formation because the endothermicity of this reaction is small and steric ratio is high. This paper considers the use of allene as the initiator of chain-radical reactions of pyrolysis.
Keywords: pyrolysis, propadiene (allene), radical chain reactions.

1 Introduction

About 140 MM tons of ethylene was produced worldwide in 2012 utilizing over 400 MM tons of raw material. Improved ethylene selectivity is very important in view of the growing demand of monomers. This paper demonstrates that allene significantly increases the initiation rate of pyrolysis radical chain reactions and thereby increasing the yield of ethylene from feedstock. A process design, which requires recirculation of allene formed in the process, is proposed.

2 Influence of initiating step on the chain-radical reactions rate

The radical-chain reaction rate is $W = k_c \cdot [\overset{\bullet}{R}] \cdot [M]$, where k_c is kinetic constant of chain propagation, $[\overset{\bullet}{R}]$ – radical concentration, and $[M]$ – reacting hydrocarbons concentration. Radical concentration can be calculated by condition of equality of rates of initiation and destruction of radicals, $W_i = k_r \cdot [\overset{\bullet}{R}]^2$, where W_i is the initiation rate and k_r – the radicals recombination-rate constant. Therefore, radical concentration is $[\overset{\bullet}{R}] = \sqrt{\dfrac{W_i}{k_r}}$. Thus, the pyrolysis radical-chain reaction rate is $W = k_c \cdot \sqrt{\dfrac{W_i}{k_r}} \cdot [M]$, so it is proportional with W_i.

The rate constant of allene reaction with alkanes is estimated by activation energy (E) in the range from 113 to 182 kJ and a minimum steric factor p of 0.1 [1]. The rate of radicals formation resulting in reactions $C_3H_4 + C_3H_6$, $C_3H_4 + C_3H_8$ are much faster than the chains initiated during unimolecular decomposition of propane and propylene having an activation energy E in the range from 354 to 360 kJ [1–3]. This is explained by relatively low activation energies of bimolecular reactions.

Let us consider a low conversion pyrolysis reaction of propane (propylene concentration is 0.1 mol %). 1 mol % of allene is injected in the raw material.
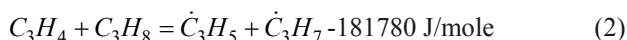
Chain initiation stage can be the following (1):

$$C_3H_4 + C_3H_6 = 2\dot{C}_3H_5 - 113000 \text{ J/mole} \tag{1}$$

Reaction (1) rate:

$$W_1 = k_1 \cdot [C_3H_4] \cdot [C_3H_6] = 10^{-11} \cdot e^{-\frac{113000}{RT}} \cdot 10^{17} \cdot 10^{16} \text{ molecule} \cdot \text{cm}^{-3} \cdot \text{sec}^{-1}.$$

Initiation can also take place according to reaction (2):

$$C_3H_4 + C_3H_8 = \dot{C}_3H_5 + \dot{C}_3H_7 - 181780 \text{ J/mole} \tag{2}$$

Reaction (2) rate:

$$W_2 = k_2 \cdot [C_3H_4] \cdot [C_3H_8] = 10^{-11} \cdot e^{-\frac{181780}{RT}} \cdot 10^{17} \cdot 10^{19} \text{ molecule} \cdot \text{cm}^{-3} \cdot \text{sec}^{-1}.$$

The third option of initiation is propane unimolecular decomposition:

$$C_3H_8 = \dot{C}_2H_5 + \dot{C}H_3 \ -354000 \text{ J/mole} \tag{3}$$

Reaction (3) rate:

$$W_3 = k_3 \cdot [C_3H_8] = 10^{15} \cdot e^{-\frac{354000}{RT}} \cdot 10^{19} \text{ molecule·cm}^{-3} \cdot \text{sec}^{-1}.$$

Rates for initiating reactions (1)-(3), respectively (4)–(6):

$$W_1 = 10^{22} \cdot e^{-\frac{113000}{RT}} \text{ molecule·cm}^{-3} \cdot \text{sec}^{-1}; \tag{4}$$

$$W_2 = 10^{25} \cdot e^{-\frac{181780}{RT}} \text{ molecule·cm}^{-3} \cdot \text{sec}^{-1}; \tag{5}$$

$$W_3 = 10^{34} \cdot e^{-\frac{354000}{RT}} \text{ molecule·cm}^{-3} \cdot \text{sec}^{-1}. \tag{6}$$

Activation energies were determined from heat effects of reactions [1, 3].

Chain initiation rates for these reactions at different temperatures are shown in Table 1.

It is shown that at temperatures below 1000 K initiation in reactions with allene is much faster than the reaction of propane unimolecular decomposition. Reaction of allene and propylene proceeds with high speed even at very low concentrations of propylene.

Table 1: The rate of initiation by the reactions (1) – (3), molecule·cm^{-3}·sec^{-1}.

T, K	$C_3H_4 + C_3H_6 = 2\dot{C}_3H_5$	$C_3H_4 + C_3H_8 = \dot{C}_3H_5 + \dot{C}_3H_7$	$C_3H_8 = \dot{C}_2H_5 + \dot{C}H_3$
1110	$10^{16.679}$	$10^{16.400}$	$10^{17.331}$
1053	$10^{16.384}$	$10^{15.965}$	$10^{16.405}$
1000	$10^{16.088}$	$10^{15.489}$	$10^{15.479}$
900	$10^{15.443}$	$10^{14.452}$	$10^{13.459}$
833	$10^{14.906}$	$10^{13.587}$	$10^{11.775}$

Allene is produced during pyrolysis at the highest temperatures in the following reaction: $C_3H_6 \rightarrow \dot{C}_3H_5 + \dot{H} \rightarrow C_3H_4 + \dot{H}$.

Allene formation can proceed only at high temperatures, when allene evinces no initiating ability and has no influence on the process, due to the high endothermicity of the allyl radical's dissociation.

3   Experimental study of allene effect on pyrolysis process

Recirculation of allene formed during pyrolysis can improve process efficiency. When allene is injected into pyrolysis feedstock, the product balance changes due to the initiating action of allene. The authors carried out petrol pyrolysis with and without the addition of allene. The results are shown in Tables 2–4.

As seen from the tables below, the yield of ethylene was raised by up to a relative 10% due to the initiating effect of allene. Yield of the target gaseous products of pyrolysis is accompanied by a reduction of liquid products yield.

Table 2: Results of naphtha pyrolysis (fraction 85−150°C), feedstock to inert diluent (helium) ratio is 1 : 3.66 mole/mole.

Pyrolysis products	Pyrolysis products yield, % wt per raw material	
	w/o allene, pyrolysis time 0.5 sec	0.3 % wt of allene, pyrolysis time 0.05 sec
Temperature 820°C		
C_2H_4	33.0	35.5
C_3H_6	15.0	16.4
C_4H_6	5.0	9.0
Temperature 790°C		
C_2H_4	27.0	29.5
C_3H_6	15.0	16.4
C_4H_6	6.0	10.0

Table 3: Outputs of main products for pyrolysis of fractions 70–100°C of gasoline raffinate, at 820°C, 0.1 MPa, pyrolysis time 1 sec, ratio of raw material to inert diluent (helium) is 1: 3.66 mole/mole.

Allene added, % wt per raw material	Output, % wt per raw material		
	C_2H_4	C_3H_6	C_{5+}
0.0	24.7±0.7	12.3±0.2	22.3±0.6
0.3	27.3±0.2	13.2±0.7	19.1±0.6
0.5	27.8±0.3	13.6±0.6	17.3±0.5

Table 4: Allene influence on pyrolysis of gasoline fraction 70−140°C with helium as diluent in the ratio 1 : 3 mole/mole of raw material.

Temperature, °C	Pyrolysis time, sec	Allene adding, % wt	Output, % wt per raw material			
			C_2H_4	C_3H_6	C_4H_6	C_{5+}
835	0.5	0.0	32.9	20.5	4.3	9.5
835	0.5	1.0	35.3	21.4	5.8	8.8
800	1.0	0.0	30.5	19.9	3.7	18.8
800	1.0	1.0	32.5	21.7	4.4	14.8

Fig. 1 shows the proposed by authors process flow diagram of pyrolysis.
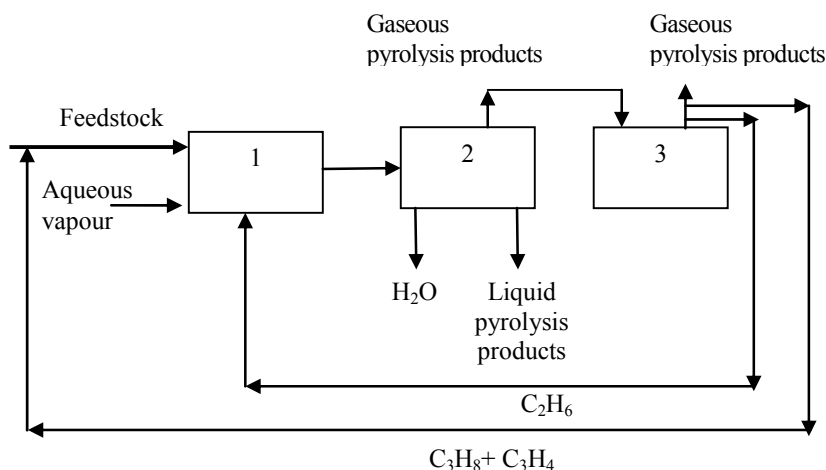
Figure 1:   Pyrolysis flow chart: 1 – pyrolysis furnaces section; 2 – recovery of liquid products; 3 – unit of gaseous products' rectification.

The resulting allene is entirely recycled as part of a mixture with propane, which is injected into the feedstock.

4   Conclusion

Recirculation of allene will improve ethylene yield by up to a relative 10% by means of the initiating action of allene and in addition by pyrolysis of propane. Furthermore, recirculation of propane increases ethylene yield.

The yield of liquid products of condensation decreases, apparently due to the fact that its formation occurs partly by molecular mechanism. Allene accelerates the radical chain reaction of pyrolysis while condensation molecular reactions remain non-accelerated. Allene may be separated in the residue of propane/propylene splitter column and arrangements for its recirculation do not require substantial capital expenses.

References

[1]   Magaril, R.Z., *Theoretical foundations of chemical refining processes: monograph,* [in Russian], KDU: Moscow, 2010.

[2]   Korzun, N.V., Magaril, R.Z., *Thermal processes of refining,* [in Russian], KDU: Moscow, 2008.

[3]   Gurvich, L.V., Karachevcev, G.V., Kondratyev, V.N. *et al., Bond opening energies. The ionization potentials and electron affinities,* [in Russian], Nauka: Moscow, 1974.