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Thermal Cracking Furnace Optimal Modeling Based on Enriched Kumar Model by Free-Radical Reactions

Peng Mu ^{1,2} and Xiangbai Gu ^{1,2,3,*}¹ College of Information Science & Technology, Beijing University of Chemical Technology, Beijing 100029, China; moupeng@mail.buct.edu.cn² Engineering Research Center of Intelligent PSE, Ministry of Education of China, Beijing 100029, China³ Sinopec Engineering (Group) Co., Ltd., Beijing 100029, China

* Correspondence: 2016400137@mail.buct.edu.cn

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Abstract: The Kumar model as a molecular model has achieved successful application. However, only 22 reactions limit its veracity and adaptability for feedstocks. A series of models with different degrees of integration of the free radical model and the molecular model has been proposed to enhance feedstock adaptability and simulation accuracy. An improved search engine algorithm, namely Improved PageRank (IPR), is provided and applied to calculate the importance of substances in Kumar model to screen the free-radical reaction network for efficient model selection. A methodology of optimal structure and model parameters chosen is applied to the target to improve the adaptability of the material and the accuracy of the model. Then, two cases with different feedstocks are demonstrated with industrial data to verify the correctness of the proposed approach and its wide feedstock adaptability. The proposed model demonstrates good performance: (1) The mean relative errors (MRE) of the K-R (Kumar and free-radical) model have reached an order of magnitude less than 0.1% compared with 5% in the Kumar model. Further, (2) the K-R model can be implemented to model some feedstocks which Kumar model can't simulate successfully. The K-R model can be applied in simulation of extensive feedstocks with high accuracy.

Keywords: reaction network enrichment; K-R model; improved pagerank algorithm (IPR); model-fitting; kinetics

1. Introduction

Ethylene is an important olefinic hydrocarbon in the petrochemical industry, while pyrolysis is the major available industrial process exists for the production of olefins yet although some research has been performed on catalytic cracking for the production of such materials [1–7]. Traditionally, the feedstock used is petroleum fraction, although some reports say biomass fuel have been used to produce such materials, the industrialization is limited [8–12]. The modern ethylene plant usually has a yield of billions of pounds (about million tons) per year, in which even a trace of deviation in simulation may have significant influence on the economy and environment [13,14]. So, an accurate model is always welcomed. The work of modeling a furnace can be mainly divided into several parts [15], the reaction modeling, the reactor modeling [16,17], the burner modeling [18] and the coking modeling [19,20], of which the reaction model is the more central part. In this work, the assumption of a clean tube is adopted. For the modeling of the reactor and burner, a one-dimensional reactor model was used with the model and parameters obtained from previous research in our lab [21]. There are two kinds of reaction model: one is the empirical model and the other is the mechanism model. The empirical model contains the statistical response surface methodology [22] and sensitivity equation [23], lumping method with parameters estimation [24], and the artificial intelligence model [25].

For the reason that they don't reflect the basic reaction theory, the accuracy of data-driven models cannot be guaranteed in areas not covered by modeling data, thus, their extensionality in hazardous chemical industry is limited. It can be applied as a first estimation [26]. Mechanism model can be divided into molecular model and the free-radical model. The characters of molecular model are simple but inaccurate while the free-radical model is the opposite [27,28].

The free-radical theory was proposed in the 1930s and is considered as the approach which describes the nature of pyrolysis reactions [29–32]. Detailed models and parameters have been developed for free radical pyrolysis kinetics of hydrocarbons with a single component [33]. However, such models are limited to the poor calculation ability of computers, and thus their application in the decomposition of petroleum-based feedstocks has been under restriction [34]. Available methods include simplifying the raw material based on a pseudo component approach [26], simplifying the reaction network by analyzing it [35,36], and removing unnecessary reactions based on the feed composition. These ways must rebuild the model when the raw material changes, which is inconvenient. From another point of view, the obstacles of reconstructing of the raw material based on the business data are not well solved yet. At present, the error in reconstructing the raw material from commercial data remains large, especially for the petroleum product [37].

The molecular model was proposed in the early 1970s. For lighter feedstocks, the work of Froment [38,39] and co-authors provides reliable predictions. In China, due to the limitation of light feedstocks, naphtha is mainly used. For petroleum-based feedstocks, the Kumar model proposed by Kumar & Kunzru in 1985 [40] is still one of the popular molecular approaches in modeling decomposition of petroleum-based feedstocks in the past 30 years. In the Kumar model, the first-order reaction is proposed to express the composition of raw materials and reactions among heavy components. The initial selectivity of the first-order reaction is optimized to adapt different feedstocks. For the reason that the secondary reactions don't change with the raw materials, it still gets researchers' attention in recent years. Zhang and Chen proposed a coefficient optimizing method based on Shannon entropy in 2012 [41]. Cui used the chaos optimization method to determine the coefficient [21]. However, all these researchers mainly focus on the algorithm of optimization and neglect the main problem of the molecular model itself. When optimizing, sometimes, it runs into the local optimal, and thus more complicated algorithms need to be employed and this takes more time, which limits the model's application in online simulation. Moreover, it can't get a reasonable solution sometimes. This is because simplifying a complex free-radical reaction network to a molecule reaction network with twenty-odd reactions may miss some phenomena like co-pyrolysis [42,43]. Co-pyrolysis is a phenomenon whereby different feedstocks are cracked together, and the product yield will be different compared to when they are cracked respectively. This is usually explained by the theory of banishing of free radicals which can't be describe by molecular model.

Lumping methods with parameters estimation are also important methods for modeling the pyrolysis of petroleum-based feedstocks. They used virtual components to describe the raw materials and used parameter estimation as a tool to deal with the different properties of the raw materials [44–46]. As the properties of the feedstock change, the reaction parameters also change, so the method is suitable for evaluating the reaction properties of a particular feedstock. However, when modeling an industrial device that the feedstock constantly changes, it is not convenient.

To provide a variety of alternative models for different materials to overcome the disadvantages of a single model, a new K-R (Kumar and free-radical) model is proposed. The aim of the approach is to find a way that is both accurate and efficient. Section 2 introduces the method of enriching the Kumar model with free-radical approach and new K-R structural framework. Section 3 introduces the process of model-fitting: Firstly, the optimal structure is found based on an improved PR algorithm and a traversal MRE (mean relative error) calculation. This is a widely used algorithm in analyzing complex network [47,48] Secondly, the parameters of the model are optimized to accommodate different feedstock and to increase the accuracy of modeling. In Section 4, two cases are implemented to verify

the feedstock adaptability and efficiency of the K-R model. The conclusions and recommendations are summarized in Section 5.

2. The Method and Basic Structural Framework of K-R Model

2.1. The Method of Enriching the Kumar Model with Free-Radical Approach

In order to solve the problem brought by co-pyrolysis [42], a newly proposed hybrid model called K-R model is established. The core idea of K-R (enriched Kumar model with free-radical approach) is enriching the Kumar model with free-radical approach. In the Kumar model [40], listed as Table 1, the first order reaction should be unchanged. The reasons are as follows:

- (1). The first-order reaction (No.1 in Table 1) is the key merit of Kumar model which solved the insolvable problem of reconstructing the feedstock in free-radical approach [37].
- (2). The first-order reaction is convenient in optimizing the model to adapt to the change of raw material [40].
- (3). The approach of pyrolysis is aimed at acquiring light olefin from heavier products from the petroleum industry. For the reason that the first-order reaction is mainly linked with the heavy components reaction network, it is not necessary to be enriched.

Table 1. Kumar model.

No.	Reactions	E,kcal/g·mol	k_0, s^{-1}
1	naphtha $\rightarrow 0.58H_2 + 0.68CH_4 + 0.88C_2H_4 + 0.1C_2H_6 + 0.6C_3H_6 + 0.02C_3H_8 + 0.035C_4H_{10} + 0.2C_4H_8 + 0.07C_4H_6 + 0.09C_{4+}$	52.58	6.565×10^{11}
2	$C_2H_6 \rightarrow C_2H_4 + H_2$	65.21	4.652×10^{13}
3	$C_3H_6 \rightarrow C_2H_2 + CH_4$	65.33	7.284×10^{12}
4	$C_2H_2 + C_2H_4 \rightarrow C_4H_6$	41.26	1.026×10^{15}
5	$2C_2H_6 \rightarrow C_3H_8 + CH_4$	65.25	3.75×10^{12}
6	$C_2H_6 + C_2H_6 \rightarrow C_3H_6 + CH_4$	60.43	7.083×10^{16}
7	$C_3H_8 \rightarrow C_3H_6 + H_2$	51.29	5.888×10^{10}
8	$C_3H_8 \rightarrow C_2H_4 + CH_4$	50.6	4.692×10^{10}
9	$C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6$	59.06	2.536×10^{16}
10	$2C_3H_6 \rightarrow 3C_2H_4$	64.17	7.386×10^{12}
11	$2C_3H_6 \rightarrow 0.3C_nH_{2n-6} + 0.14C_6 + 3CH_4$	56.90	2.424×10^{11}
12	$C_3H_6 + C_2H_6 \rightarrow 1-C_4H_8 + CH_4$	60.01	1.0×10^{17}
13	$n-C_4H_{10} \rightarrow C_3H_6 + CH_4$	59.64	7.0×10^{12}
14	$n-C_4H_{10} \rightarrow 2C_2H_4 + H_2$	70.68	7.0×10^{14}
15	$n-C_4H_{10} \rightarrow C_2H_4 + C_2H_6$	61.31	4.099×10^{12}
16	$n-C_4H_{10} \rightarrow 1-C_4H_8 + H_2$	62.36	1.637×10^{12}
17	$1-C_4H_8 \rightarrow 0.41C_nH_{2n-6} + 0.19CH_6 +$	50.73	2.075×10^{11}
18	$1-C_4H_8 \rightarrow C_4H_6 + H_2$	50.00	1.0×10^{10}
19	$C_2H_4 + C_4H_6 \rightarrow B + 2H_2$	34.56	8.385×10^{12}
20	$C_4H_6 + C_3H_6 \rightarrow T + 2H_2$	35.64	9.74×10^{11}
21	$C_4H_6 + 1-C_4H_8 \rightarrow EB + 2H_2$	57.97	6.4×10^{17}
22	$2C_4H_6 \rightarrow ST + 2H_2$	29.76	1.51×10^{12}

The details of the adopted free-radical reaction network is showed in Table 2.

In Table 2, The “*” after the substance means it is free radical. The substances involved in the Kumar model are shown in Table 3.

Table 2. Free-radical network and its parameters [49].

Reactions	E _a Kcal/mol	Log ₁₀ A; L/mol·s	2-C ₃ H ₇ *→H * + C ₃ H ₆	38.70	13.30
C ₂ H ₆ →CH ₃ * + CH ₃ *	87.5	16.57	C ₄ H ₇ *→H * + C ₄ H ₆	49.30	14.10
C ₃ H ₈ →CH ₃ * + C ₂ H ₅ *	85.0	16.30	C ₄ H ₇ *→C ₂ H ₃ * + C ₂ H ₄	35.15	11.00
2C ₂ H ₄ →C ₂ H ₃ * + C ₂ H ₅ *	65.0	13.95	1-C ₄ H ₉ *→H * + 1-C ₄ H ₈	36.60	13.00
C ₃ H ₆ →CH ₃ * + C ₂ H ₃ *	95.0	17.90	1-C ₄ H ₉ *→C ₂ H ₅ * + C ₂ H ₄	28.00	12.20
2C ₃ H ₆ →C ₃ H ₅ * + 1-C ₃ H ₇ *	51.0	11.54	2-C ₄ H ₉ *→CH ₃ * + C ₃ H ₆	31.90	13.40
H * + C ₂ H ₆ →H ₂ + C ₂ H ₅ *	9.70	11.08	2-C ₄ H ₉ *→H * + 1-C ₄ H ₈	39.80	13.30
H * + C ₃ H ₈ →H ₂ + 1-C ₃ H ₇ *	9.70	11.00	2-C ₄ H ₉ *→H * + 2-C ₄ H ₈	37.90	12.70
H * + C ₃ H ₈ →H ₂ + 2-C ₃ H ₇ *	8.30	10.95	C ₅ H ₉ *→CH ₃ * + C ₄ H ₆	38.00	12.90
H * + C ₂ H ₄ →H ₂ + C ₂ H ₃ *	4.00	8.50	C ₅ H ₉ *→C ₂ H ₃ * + C ₃ H ₆	34.00	13.20
H * + C ₃ H ₆ →H ₂ + C ₃ H ₅ *	4.50	8.50	C ₅ H ₉ *→C ₃ H ₅ * + C ₂ H ₄	34.00	13.20
CH ₃ * + C ₂ H ₆ →CH ₄ + C ₂ H ₅ *	15.25	10.20	1-C ₅ H ₁₁ *→C ₂ H ₄ + 1-C ₃ H ₇ *	32.70	13.70
CH ₃ * + C ₃ H ₈ →CH ₄ + 1-C ₃ H ₇ *	12.70	10.10	2-C ₅ H ₁₁ *→C ₂ H ₅ * + C ₃ H ₆	29.10	12.70
CH ₃ * + C ₃ H ₈ →CH ₄ + 2-C ₃ H ₇ *	10.80	10.10	H * + CH ₃ *→CH ₄	0	9.86
CH ₃ * + C ₂ H ₄ →CH ₄ + C ₂ H ₃ *	13.00	8.60	H * + C ₂ H ₃ *→C ₂ H ₄	0	10.00
CH ₃ * + C ₃ H ₆ →CH ₄ + C ₃ H ₅ *	4.50	7.30	H * + C ₃ H ₅ *→C ₃ H ₆	0	10.30
C ₂ H ₅ * + C ₃ H ₈ →C ₂ H ₆ + 1-C ₃ H ₇ *	12.60	8.70	H * + C ₂ H ₅ *→C ₂ H ₆	0	10.50
C ₂ H ₅ * + C ₃ H ₈ →C ₂ H ₆ + 2-C ₃ H ₇ *	10.40	8.70	H * + 1-C ₃ H ₇ *→C ₃ H ₈	0	10.00
C ₂ H ₅ * + C ₂ H ₄ →C ₃ H ₆ + CH ₃ *	19.00	9.15	H * + 2-C ₃ H ₇ *→C ₃ H ₈	0	10.00
C ₂ H ₅ * + C ₃ H ₆ →C ₂ H ₆ + C ₃ H ₅ *	9.20	8.65	H * + 1-C ₄ H ₉ *→n-C ₄ H ₁₀	0	10.00
C ₂ H ₅ * + C ₃ H ₈ →C ₂ H ₄ + C ₃ H ₅ *	14.50	10.20	H * + 2-C ₄ H ₉ *→n-C ₄ H ₁₀	0	10.00
C ₃ H ₅ * + C ₃ H ₈ →C ₃ H ₆ + 1-C ₃ H ₇ *	18.80	9.00	H * + C ₄ H ₇ *→1-C ₄ H ₈	0	10.30
C ₃ H ₅ * + C ₃ H ₈ →C ₃ H ₆ + 1-C ₃ H ₇ *	16.20	8.90	H * + C ₅ H ₉ *→C ₅ H ₁₀	0	10.34
H * + C ₂ H ₄ →C ₂ H ₅ *	1.30	10.65	CH ₃ * + CH ₃ *→C ₂ H ₆	0	10.00
H * + C ₃ H ₆ →1-C ₃ H ₇ *	2.90	10.00	CH ₃ * + C ₂ H ₅ *→C ₃ H ₈	0	10.00
H * + C ₃ H ₆ →2-C ₃ H ₇ *	1.50	10.00	CH ₃ * + 1-C ₃ H ₇ *→n-C ₄ H ₁₀	0	9.51
H * + C ₂ H ₂ →C ₂ H ₃ *	1.30	10.60	CH ₃ * + 2-C ₃ H ₇ *→n-C ₄ H ₁₀	0	9.51
H * + C ₃ H ₄ →C ₃ H ₅ *	1.50	10.00	CH ₃ * + 1-C ₄ H ₉ *→C ₅ H ₁₂	0	10.11
H * + C ₄ H ₆ →C ₄ H ₇ *	1.30	10.60	CH ₃ * + C ₂ H ₃ *→C ₃ H ₆	0	10.86
CH ₃ * + C ₂ H ₄ →1-C ₃ H ₇ *	7.80	8.60	CH ₃ * + C ₃ H ₅ *→1-C ₄ H ₈	0	11.00
CH ₃ * + C ₃ H ₆ →2-C ₄ H ₉ *	7.40	8.51	CH ₃ * + C ₄ H ₇ *→C ₅ H ₁₀	0	9.51
CH ₃ * + C ₄ H ₆ →C ₅ H ₉ *	4.10	7.90	C ₂ H ₅ * + C ₂ H ₅ *→n-C ₄ H ₁₀	0	8.60
C ₂ H ₅ * + C ₂ H ₄ →1-C ₄ H ₉ *	7.60	7.80	C ₂ H ₅ * + 1-C ₃ H ₇ *→n-C ₅ H ₁₂	0	8.90
C ₂ H ₅ * + C ₃ H ₆ →2-C ₅ H ₁₁ *	7.50	7.50	C ₂ H ₅ * + C ₂ H ₃ *→1-C ₄ H ₈	0	9.00
1-C ₃ H ₇ * + C ₂ H ₄ →1-C ₅ H ₁₁ *	7.40	7.80	C ₂ H ₅ * + C ₃ H ₅ *→C ₅ H ₁₀	0	9.51
C ₂ H ₃ * + C ₂ H ₄ →C ₄ H ₇ *	7.65	7.65	C ₂ H ₅ * + C ₂ H ₃ *→C ₄ H ₆	0	8.00
C ₂ H ₃ * + C ₃ H ₆ →C ₅ H ₉ *	8.00	7.00	C ₂ H ₅ * + C ₂ H ₅ *→C ₂ H ₆ + C ₂ H ₄	0	7.70
C ₃ H ₅ * + C ₂ H ₄ →C ₅ H ₉ *	8.00	7.00	C ₂ H ₅ * + C ₃ H ₅ *→C ₂ H ₆ + C ₃ H ₄	0	8.60
C ₂ H ₃ *→H * + C ₂ H ₂	31.50	9.30	C ₂ H ₅ * + C ₃ H ₅ *→C ₂ H ₄ + C ₃ H ₆	0	8.60
C ₂ H ₅ *→H * + C ₂ H ₄	40.90	13.90	C ₂ H ₅ * + C ₄ H ₇ *→C ₂ H ₆ + C ₄ H ₆	0	9.11
C ₃ H ₅ *→H * + C ₃ H ₄	48.00	12.84	C ₂ H ₅ * + C ₄ H ₇ *→C ₂ H ₄ + 1-C ₄ H ₈	0	8.51
C ₃ H ₅ *→CH ₃ * + C ₂ H ₂	36.00	10.48	C ₃ H ₅ * + C ₄ H ₇ *→C ₃ H ₆ + C ₄ H ₆	0	10.00
1-C ₃ H ₇ *→H * + C ₃ H ₆	38.40	13.30	C ₃ H ₅ * + C ₄ H ₇ *→C ₃ H ₄ + 1-C ₄ H ₈	0	9.00
1-C ₃ H ₇ *→CH ₃ * + C ₂ H ₄	34.00	13.70	C ₄ H ₇ * + C ₄ H ₇ *→C ₄ H ₆ + 1-C ₄ H ₈	0	9.51

Table 3. List of relevant substance.

Rank of Species (j)	Substance	5	C ₂ H ₆	10	C ₄ H ₆	15	n-C ₄ H ₁₀
1	Naphtha	6	C ₃ H ₆	11	C ₄ ⁺	16	B
2	H ₂	7	C ₃ H ₈	12	C ₂ H ₂	17	T
3	CH ₄	8	C ₄ H ₁₀	13	C _n H _{2n-6}	18	EB
4	C ₂ H ₄	9	C ₄ H ₈	14	i-C ₄ H ₈	19	ST

To enrich the whole secondary reaction network is also not efficacious because: (1) The difficulty and computation cost in building a free-radical network is due to the exponential growth with the amount of carbon [32,50]. (2) Most reactions of heavy components are calculated in the first-order reaction whereby a large-scale free-radical network linked with heavy components reactions network may result in double counting, which may increase the error of the whole K-R model. (3) Ethylene factory now mainly focus on the product yield of high value-added hydrocarbon of which the carbon number is less than or equal to 4.

For the complementing free-radical network, the following must be taken into consideration:

- (1). Reactions of heavier reactant still have great influence on reactions among the lighter ones.
- (2). Double counting with the Kumar model must be avoided.

- (3). The reactions of reactants of the same carbon number coupled with each other greatly.

So, the whole free-radical reaction network will be retained completely. Only the output of the free-radical reaction network should be screened together with the modification in the Kumar model to avoid double counting.

The details of the Kumar reaction network are shown in Table 1 [28].

2.2. The Basic Framework of K-R Model and K-R Structure

The K-R model contains two parts mainly. The first one is a modified Kumar model. Its first-order reaction is completely retained, and the other reactions are pruned. The other one is a free-radical reaction network with the reactions complete and its output partly retains. The modification of Kumar model and the output of the free-radical network is decided by a structural parameter S_p which means substances of how many C elements will be screened for enriching. The framework and mathematical relations are presented in Figure 1.

Figure 1. The loop iteration of the K-R model.

In Figure 1, each part means an infinitesimal part of the tube. Start from $I = 0$ and end at $I = \frac{L}{l}$. The L means the length of the tube. The ' l ' means the length of the infinitesimal part and it should be as small as possible (0.01 m in this research). For the first infinitesimal part, the input is the composition of feedstock. It is presented by a vector quantity (19×1) of which the congruent relationship is shown in Table 3. The temperature T_i and pressure P_i are calculated based on one-dimensional reactor model. The output of the first part is $\vec{f}_r(1)$ and $\vec{f}_{kr}(1)$. The details of function relationship are recommended in Figure 2. For the other parts, the input are $\vec{f}_r(i)$ and $\vec{f}_{kr}(i)$ from last iteration and the output are $\vec{f}_r(i+1)$ and $\vec{f}_{kr}(i+1)$. Once the reactions have reach the end ($I = \frac{L}{l}$), $\vec{f}_{kr}(\frac{L}{l} + 1)$ will be exported as the product yield. The $\vec{f}_r$ and $\vec{f}_{kr}$ mentioned above are all vector quantities (19×1) which can be refer to Table 3.

Figure 2. The K-R model (reaction model).

With respect to the reaction model, it has four types corresponding to different S_p values. The S_p value means the carbon number of heaviest substances been screened for enriching. They are showed in Figure 2. S_p can be 1, 2, 3 and 4 of which the reason is that in the Kumar model only reactions among light constituents are discussed emphatically.

The details of the enriched structure for $S_p = 1$ to 4 is demonstrated in Figure 2.

In Figure 2, the main differences with different S_p values are calculations of the output of the modified Kumar model $f_{kr}(i-1)$ and the output of free-radical approach $f_r(i)$. They are also 19×1 , which can be refer to Table 3. Take $S_p = 4$ for example, due to substances which lighter than C_4^+ will be calculated by free-radical approach, the modified Kumar model only calculate the residual substance as naphtha, C_4^+ , B, T, EB, ST. The reactions should also be modified to avoid double counting which, will be explained in Section “Modification of Kumar Model”. The methodology of how to decide on the optimal S_p value is shown in Section 3.

In each sub-graph, the functional relationships in Figure 2 are presented below, it is an element of the loop iteration process showed in Figure 1. For $(I-1)$, the infinitesimal part, its input is $f_{kr}(i-1)$, $f_r(i-1)$ and its output is $f_{kr}(i)$ and $f_r(i)$. The $f_{kr}(i)$ means at $(i-1)$ th infinitesimal part, the content of different substances listed in Table 3. Its initial value is feedstock. f_{kr} is a vector quantity of 19×1 . The K-R model contains three part mainly:

- (1). The first-order reaction.
- (2). The modified secondary reactions
- (3). The supplied free-radical reaction network

For the first-order reaction, it is same with the NO.1 reaction in Kumar model in Table 1. The result of (1) and (2) is represented as $\vec{f}_{k'}(i-1)$. $\vec{f}_{k'}(i)$ is also a vector quantity of 19×1 (refer to Table 3) and is concerned with S_p value.

The result of Equation (3), $\vec{f}_r$ (also 19×1), means the changes of contents calculated by the free-radical approach listed in Table 2. Simulation of reactions obey the law of Arrhenius.

For the modified Kumar model,

$$\vec{f}_{k'}(i) = \varphi_{k'}(\vec{f}_{kr}(i-1), S_p) \quad (1)$$

where function $\varphi_{k'}$ refers to the modified Kumar model which is pruned from Table 1 with the approach presented in Section “Modification of Kumar Model” (change with S_p value). Briefly, it is a Kumar model in which some reactions has been removed or modified with S_p value. The $\vec{f}_{k'}(i)$ (19×1) is the substances variation calculated by the modified Kumar model. The i is the number of infinitesimal parts which have been introduced above.

For the supplied free-radical reaction network,

$$\vec{f}'_r(l) = \varphi_r(\vec{f}'_k(i-1), \vec{f}_r(i-1), S_p) \quad (2)$$

where φ_r refer to the free-radical reaction network listed in Table 2. The $\vec{f}'_k(i-1)$ is the output of modified Kumar model. The $\vec{f}_r(i-1)$ is the content of free radicals of which the initial value is 0 and changes with the iteration. Its dimensionality equal to the amount of free-radicals listed in Table 2. $\vec{f}'_r(i)$ is the result of the free-radical approach, which is 19×1 . This is influenced by the S_p value, which refers to Table 4.

Table 4. S_p value and the structure of K-R model.

S_p Value		1	2	3	4
Content been calculated by-	Residual Kumar model	Naphtha, C_2H_6 , C_2H_2 , C_3H_8 , C_4H_6 , C_4H_8 , C_4H_{10} , C_4^+ , B, T, EB, ST	Naphtha, C_3H_8 , C_4H_6 , C_4H_8 , C_4H_{10} , C_4^+ , B, T, EB, ST	Naphtha, C_4H_6 , C_4H_8 , C_4H_{10} , C_4^+ , B, T, EB, ST	Naphtha, C_4^+ , B, T, EB, ST
	Free-radical approach	H_2 , CH_4 , C_2H_4 , C_3H_6	H_2 , CH_4 , C_2H_4 , C_3H_6 , C_2H_6 , C_2H_2	H_2 , CH_4 , C_2H_4 , C_3H_6 , C_2H_6 , C_2H_2 , C_3H_8	H_2 , CH_4 , C_2H_4 , C_3H_6 , C_2H_6 , C_2H_2 , C_3H_8 , C_4H_6 , C_4H_8 , C_4H_{10}

The three outputs are summarized together to be $\vec{f}_{kr}(i)$ (19×1).

Modification of Kumar Model

Before enriching the Kumar model with the free-radical approach, the Kumar model must be pruned in order to avoid double counting. So, the scope of enriched reactions must be screened first.

For the reasons:

- (1). The reactions of reactants of the same carbon number coupled with each other greatly.
- (2). The substances of ethylene (C_2H_4) and propylene (C_3H_6) are desired final products, which must be calculated by the free-radical approach.

The S_p value and the scope of substances enriched are shown in Table 4.

The methodology of obtaining the optimal S_p value is introduced in Section 3. The secondary reactions of the Kumar model should be pruned in three conditions:

- (1). Remove: when all the reactants belong to the scope
- (2). Partly Retain: Some of the reactant of the reactions belong to the scope
- (3). Retain: All the reactant are out of the scope

Notice that, for the partly retained reactions, the reaction rate should be computed as they are not removed.

3. Optimal Modeling of K-R Model

The optimal modeling of K-R model contains 2 parts: (1) The structural optimization in order to decide the scope of the enriched reactions and (2) the parameter optimization in which the initial selectivity of the first order reaction are optimized [21]. The I_s value is stoichiometric numbers in the first-order reaction in Kumar model. There are 10 I_s of which the initial numbers are acquired by sensitivity analysis. The initial values are calculated by sensitivity analysis illustrated in the paper of Kumar [29]. The target of two parts are both lowest error. $I_s(1)$ refer to stoichiometric number of H_2 in the first-order reaction of which the initial value is 0.58. $I_s(2)$ refer to CH_4 . $I_s(3)$ refer to C_2H_4 . $I_s(4)$ refer to C_2H_6 . $I_s(5)$ refer to C_3H_6 . $I_s(6)$ refer to C_3H_8 . $I_s(7)$ refer to C_4H_{10} . $I_s(8)$ refer to C_4H_8 . $I_s(9)$ refer to C_4H_6 and $I_s(10)$ refers to C_4^+ . They are representations of feedstocks. When they change, f_r , f_r' , f_k' , f_{kr} , and φ_r will change accordingly.

The optimization of the structure is screening the reactions been enriched essentially. A parameter S_p is then introduced as the representation of the structure of the model. If the S_p becomes large, the scope of substance been calculated by the free radical network will be larger, and the scope calculated by the residual Kumar model will be smaller. Also, the model will be more complex and precise. That is to say, the problem must be considered in both two ways: The first is the reactions be enriched should cover important part of Kumar model (minimal S_p value). The second is the structure must be the most suitable one in modeling of thermal cracking furnace, precise enough but not over complex (optimal S_p value). In another way, the optimal S_p is a compromise of the veracity and complexity of the model.

Due to the characteristics of the free-radical reaction network listed in Section 2.1, the scope of reactions enriched should be discretization by their carbon numbers. In this way, the robustness is also improved. The structure parameter S_p is then defined as the carbon number of the heaviest substance been enriched in K-R model. It also decides the output of the free-radical network. Table 4 indicates how S_p value decides the structure of K-R model. The maximal S_p value is 4 for the reason that, in Table 3, the carbon number of the main substances are below or under 4. It is also the scope of high value-added products which are focus by plants.

Ordinary, the value-added substance like ethylene (C_2H_4) and propylene (C_3H_6) are desired final products. So for each S_p value, calculation of substance C_2H_4 and C_3H_6 should be executed by free-radical approach. The methodology of finding minimal S_p value and optimal value is showed in Section 3.1

After optimizing the structure, the parameters of the K-R model should be optimized. The process involves adjusting the stoichiometric number of first-order reactions to improve accuracy. A fast method called SQP (Sequential Quadratic Programming) can be employed to search the optimal parameters. Also, the adaptability of feedstock are expected to be better for K-R model enriched the secondary reactions of free-radical approach. Parameter optimization is a common method to improve the adaptability and accuracy of models [51].

The modeling progress is presented in Figure 3.

Figure 3. Flowsheet of modeling in K-R model.

3.1. Structure Optimization of K-R Model

In the first part of structure optimization, in order to acquire the minimum S_p value, the importance of substances mentioned in the Kumar model (Table 3) should be calculated. So, a common Kumar model is established first. Then, an improved search engineering algorithm Improved PageRank (IPR) is employed to calculate importance of mentioned substances (Table 3). The IPR algorithm need time-depend temperature and pressure, so the length-depend data are transferred into time-depend ones. A criterion is set to ensure the S_p value covers important parts of the reaction network. After that, an MRE calculation is carried out to find the optimal S_p value. Actually, this step traverses every possible S_p value to find the structure of the minimum product yield error.

3.1.1. Minimum Scope Screened Out Via IPR Algorithm

It has been mentioned in the preceding paragraph that the reactions must be screened to determine the enriched reactions. In another word, the S_p value must be determined. To decide the S_p value, firstly, its minimum must be determined. The minimum value must ensure the free-radical network enriched the major part of Kumar model.

Zhou Fang [35,52] presented a specialized PR algorithm to calculate the importance of substance in the free-radical network. However, the algorithm has obvious shortcomings:

- (1). The original PR algorithm keeps calculating until the values converge, which means reaction equilibration [53]. However, in a thermal cracking furnace, the reactions stop before equilibration to maximize the yield of ethylene.
- (2). Zhou's PR algorithm uses the time average reaction rate to calculate the shift matrix. However, a time-dependent shift matrix may be more accurate.

Based on the above consideration, we provide an IPR algorithm to calculate the importance of substance.

Step 1: Set the initial vector quantity $\overline{IP}_0$ (19×1)

$$IP_{0,j} = \frac{C_j}{\sum_{j=1}^{19} C_j} \quad (3)$$

where $\overline{IP}_0$ is the initial vector, which is 19×1 when referring to the Kumar model. $IP_{0,j}$ indicates the initial value of substance 'j', where 'j' refers to Table 3. C_j indicates the mass fraction of a molecule of substance 'j'.

Step 1: can be comprehended as normalization.

Step 2: Calculate the shift matrix M at time ' t_m '

For a reaction network that contains reactions from R_1 to R_R (in Kumar, R_1 to R_{19}), suppose the reaction rate of reaction R_r at time m is k_{rm} with the Arrhenius equation (Equation (14)), and it has the reactant S_{reactant} and resultant $S_{\text{resultant}}$. The stoichiometric number of reaction r regarding reactant and resultant are $\alpha_{r,\text{reactant}}$ and $\alpha_{r,\text{resultant}}$ respectively. For shift matrix M for reaction r :

$$M_{r,m}(\text{reactant, resultant}) = \alpha_{r,\text{reactant}} \times k_{rm} \quad (4)$$

$$M_{r,m}(\text{resultant, reactant}) = \alpha_{r,\text{resultant}} \times k_{rm} \quad (5)$$

where both k_r and shift matrix M_m are time-dependent variables. The shift matrix is 19×19 matrix for the Kumar model. For the whole reaction network,

$$M_m = \sum_{r=1}^R M_{r,m} \quad (6)$$

In the Kumar model, R equals 22, which means there are 22 reactions in Kumar model. $M_{r,m}$ and M_m are all 19×19 in Kumar model.

The process of generating the shift matrix M can be described as Figure 4.

Figure 4. The generation of shift matrix M_m at time m .

The Kumar model only gives the profile of length-dependent temperature T_i , pressure P_i , and the flow speed v_i . The reason for this is that, for a specific furnace, the length of the tube is fixed. The data should be transformed as follows:

$$P_i = \Phi(i) \quad (7)$$

$$T_i = \Psi(i) \quad (8)$$

$$v_i = \Gamma(i) \quad (9)$$

where P_i is pressure in length 'i', Φ is the functional relationship between the length and the pressure. Ψ is the functional relationship between the length and temperature. Γ is the functional relationship between the length and flow speed. 'i' is the length variable which describes the length of the tube in a thermal cracking furnace (range from 0 to $\frac{l}{\delta}$). These relationships are all discrete. With the length-dependent flow speed, the time ΔT_i used between l_i to l_{i+1} can be calculated as Equations (10) and (11).

$$\Delta T_i = \frac{(i+1) \times l - i \times l}{v_i} = \frac{l}{v_i} \quad (10)$$

$$\begin{cases} t_\delta = \sum_{i=0}^{\delta} \Delta T_i \\ P_{t_\delta} = \frac{P_{i+1} + P_i}{2} \\ T_{t_\delta} = \frac{T_{i+1} + T_i}{2} \end{cases} \quad (11)$$

where l is the length of the infinitesimal part, while t_δ is the time costed between the 0th and δ the infinitesimal parts. In this way, the pressure P_{t_δ} and temperature T_{t_δ} at time t_δ can be obtained. Formulas (10)–(13) calculate the residual time t_m at l_{i+1} . The pressure and temperature are then corresponded to time. By calculating along the tube, we can get the relationship between time and pressure/temperature.

$$P_{t_\delta} = \Phi'(t_\delta) \quad (12)$$

$$T_{t_\delta} = \Psi'(t_\delta) \quad (13)$$

The relationships given in Formulas (12) and (13) are discrete. By interpolation, we can get the complete data of time-dependent pressure P_m and temperature T_m (at time m , $m \in [0, t_s]$, t_s is the residence time). By the Arrhenius equation, the reaction rate can be obtained:

$$\frac{d \ln(k_{m,r})}{dT_m} = \frac{E_{a,r}}{RT_m^2} \quad (14)$$

In Equation (14), $k_{m,r}$ means the reaction rate for reaction r at time m . $E_{a,r}$ is the activation energy of reaction r . T_m is the temperature at time m . R is gas constant. Then, the shift matrix M_m can be calculated.

Step 3: Calculate the IP value, as presented in Equation (15)

$$\overline{IP}_{m+1} = \frac{(1-\varepsilon)}{N} + \varepsilon \times M_m \times \Delta t \times \overline{IP}_m \quad (15)$$

where ε is the shift factor. N is the dimension of $\overline{IP}_m$, which is 22 in Kumar model, $m = 1, 2, \dots, t_r$. The Δt is the iterative time step (0.0001s in this study). The calculation will stop when ' m ' reaches the t_r (The final result is $\overline{IP}_{tr}$). The t_r is the residence time. $\overline{IP}_m$ (19×19) is the importance vector quantity which refers to Table 3.

The result of the calculation $\overrightarrow{IP}_{tr}$ means the importance of substance i .

For different S_p values, it can give the fraction of coverage for each structure. The correspondence between structure parameters and substances is listed in Table 4. A threshold value TV is need to measure the fraction of coverage. If TV become larger, the scope of reactions been enriched gets larger. Then, the model will be more complex and accurate. Otherwise, the model will be more simple and rough. In consideration of computing complexity, the TV should be no less than 80%. Then the maximum S_p value is decided. Experiments will be carried out to get the optimal S_p value for minimum error.

$$IV_{SP=k} = \sum_{j \in Scheme4_{SP=k}} IP_{tr,j} \quad (16)$$

where $IV_{SP=i}$ means the important value calculated for each S_p value. Whether $IP_{tr,j}$ (importance of substance j) should be summarized into $IV_{SP=j}$ can be found in Table 4.

$$IV_{SP=k} \geq TV \quad (17)$$

Formula (17) shows the criterion of minimum value of S_p value. The approach is presented in Figure 5.

Figure 5. The improved PR algorithm and optimal S_p value.

3.1.2. Optimal Scope of Enriched Reactions Based on MRE Analysis

An index is introduced to measure the performance of the K-R model for finding maximum scope.

$$MRE = \rho(\vec{Is}) = \sqrt[2]{\frac{\sum [(K_{\text{industry},j} - \varphi'_{kr}(\frac{l}{L}, \vec{Is})_{j, Sp=k}) / K_{\text{industry},j}]^2}{NM}} \times 100\% \quad (18)$$

where $K_{\text{industry},j}$ is the productive rate of substance j from industry data. While $\varphi'_{kr}(\frac{l}{L}, \vec{Is})_{j, Sp=k}$ is the model predicted yield. It had been mentioned above that the results $\varphi_{kr}(\frac{l}{L})$ change with $\vec{Is}$ and in this part $\vec{Is}$ is seen as a variable, t_r means the residence time with is fixed. S_p value is also fixed in this part. Not all the products are taken into consideration and the amount of substances been considered can be assigned as NM. In this case, substance which numbers as $j = 2, 3, 4, 5, 6, 9, 10$ are considered. So the $NM = 7$. Only the product yield which is larger than 1% (mass fraction) is taken into consideration. That is because, small error from low yield product may influence the final MRE greatly for MRE values the relative error.

So, the problem of parameter optimization is now adjusting the $\vec{Is}$ value to achieve minimum MRE value in conditions of different kinds of feedstock.

3.2. Parameters Optimizing

The model-fitting methods which are exercised till date for evaluating the optimum overall pyrolysis kinetics parameters usually apply traditional gradient base optimization techniques but associated with major drawback of attaining global optimum due to uncertainties in selection of initial guess [54], while the artificial approach usually consumes more time.

When studying the Kumar model, predecessors have focused on optimizing the coefficients of the first-order reaction of the Kumar model to improve precision and model adaptability to a variety of raw materials. In this way, the error in reactor modeling, the error in reaction network parameters, and the problem of reconstruction of raw materials based on commercial data can be solved at the same time. For the reason that the structure of K-R model is based on the Kumar model, the method can also be employed for the K-R model.

In previous study [21], the problem of first-order reaction can't be well solved by conventional optimization algorithm. The slow and complex optimization algorithm has to be employed to avoid falling into local optimal value. Even so, to some raw material, the algorithms still can't get a good result. This is mainly because the Kumar model itself is a molecular model. It cannot completely reflect the essence of cracking reactions. The K-R model enriched the Kumar model with free-radical reactions, which can be expected to solve the problem listed.

The optimization problem can be described as follows:

$$\min MRE = \rho(\vec{Is}) \quad (19)$$

$$\sum_{u=1}^{10} C_u \times Is(u) = C_c \quad (19-1)$$

$$\sum_{u=1}^{10} H_u \times Is(u) = H_c \quad (19-2)$$

$$Is(u) \geq 0, u = 1, 2 \dots 10 \quad (19-3)$$

where MRE is the optimal object function which can be calculated with Formula (18). Its physical meaning is the mean relative error between the model yield and the industry data. Formula (19-1) means the carbon balances, u is 1 to 10 refer to 10 initial selectivity. This has been illustrated in Section 3.

C_u is the carbon number of the substances. H_s is the hydrogen number of the substances. Formula (19-2) means the hydrogen balance. C_u and H_u mean the carbon and hydrogen corresponding to each I_s in the first order reaction in Kumar model. C_C and C_H mean the constant corresponding to carbon and hydrogen. Formula (19-3) means all the I_s are non-negative.

The optimization results are not only dependent on the optimization algorithm, but also correlated with the model itself. The optimization algorithm used in the Kumar model is too complex for the purpose of avoiding local optimum. A fast and simple algorithm may work well with the new K-R model. Moreover, the problem of modeling some raw material can be solved using the K-R. The SQP method is the canonical algorithm for the general smooth curve optimization problem. Due to the application of derivative information, it has fast convergence speed and good robustness. It is widely used in chemical simulated calculation in the past few years [55,56]. The algorithm was first proposed by Wilson in 1963 and was improved by Han S.P. [57] and Powell [56] in 1970s.

4. Case Study

4.1. Case Backgrounds and Conditions

Before building the K-R model, a Kumar model optimized by an error correction chaos algorithm [30] was built on different kinds of naphtha pyrolysis in a SL-1 furnace. Compared with other intelligent optimization algorithms (such as GA, Genetic algorithm), chaos algorithm mainly adjusts step size and optimization direction based on chaos set to avoid falling into the optimal neighborhood. By doing so, the IPR algorithm can be used to analyze the Kumar model.

The operation conditions and structural conditions of the furnace are listed as Table 5. The character parameters for the nine naphtha used are presented in Table 6.

Table 5. Structural parameters and operational conditions of type SL (Sinopec & Lummus)-1 thermal cracking furnace [21].

Structure Parameter	Value	Operational Conditions	Value
Furnace tube group	6	Feedstock flow (kg/h)	890.625
Tube pass	2	Steam/Hydrocarbon ratio	0.60
Arrangement	16/8	Coil inlet temperature (K)	875
Inner diameter (m)	0.051/0.073	Coil outlet temperature (K)	1122
Outer diameter (m)	0.063/0.086	Coil outlet pressure (kPa)	178
Length (m)	13.681/14.921		
Tube pitch (m)	0.112/0.154		

Table 6. Character parameters of naphthas (1) to (9) used.

Naphtha	1	2	3	4	5	6	7	8	9
Density (20 °C, g/cm ³)	0.6927	0.7255	0.7488	0.7022	0.7103	0.7389	0.7093	0.7375	0.6894
ASTM, °C (10%)	54.5	86.9	85.2	60	64	77	69	85.2	36.2
ASTM, °C (30%)	73	105.4	114.8	75	81	106	88	105	46.9
ASTM, °C (50%)	90	121.3	131.8	88.5	98	135	103	120.3	65
ASTM, °C (70%)	107	137.3	147.5	103	117	163	119	136.2	104.7
ASTM, °C (90%)	127	156.5	162.4	124	143	190	149	156.1	137.6
	0.7223/	0.663/	0.4631/	0.7069/	0.6669/	0.6898/	0.6409/	0.5609/	0.7379/
P/N/A	0.2234/	0.2605/	0.4856/	0.2248/	0.2605/	0.1916/	0.3172/	0.3493/	0.1742/
	0.0529	0.0762	0.0483	0.0566	0.068	0.116	0.0419	0.0893	0.0864

4.2. Structure Optimization of K-R Model

Screening the Minimum S_p Value of K-R Model by IPR Algorithm

The scope of enriched reactions is represented as S_p value. As mentioned in Section 3, the $IV_{SP=k}$ values of each S_p value should be calculated via the IPR algorithm to determine the minimal S_p value.

Firstly, the length-dependent pressure P_i and temperature T_i derived in the Kumar model are transferred into time-dependent pressure P_m and temperature T_m as the preparation for IPR calculation, which is presented in Formulas (7)–(14).

The improved PR algorithm is then carried out to calculate the importance of substance mentioned in the Kumar reaction network with Formula (15). The result of the calculation $\vec{IP}_{tr}$ value is listed in Table 7. During the process of modeling all nine naphtha with Kumar model optimized by an error correction chaos algorithm [21], naphtha (1) to (3) are strikingly different from naphtha (4) to (9). The MRE after optimization is less than 0.1% in naphtha (1) to (3) compared with which in naphtha (4) to (9). So, typically feedstock naphthas (1) and (4) are adopted as analysis objects. The results of $\vec{IP}_{tr}$ are shown in Tables 7 and 8.

Table 7. The $\vec{IP}_{tr}$ value of each substances in naphtha (1).

Substance	IP_j Value (%)	C_{4+}	5.330676
H ₂	9.397315	C ₂ H ₂	2.540632
CH ₄	14.82913	C _n H _{2n-6}	3.362184
C ₂ H ₄	19.02015	I-C ₄ H ₈	5.990581
C ₂ H ₆	4.373818	N-C ₄ H ₁₀	2.613754
C ₃ H ₆	8.31053	B	2.877133
C ₃ H ₈	2.715596	T	2.550521
C ₄ H ₁₀	2.634325	EB	2.583697
C ₄ H ₈	3.786447	ST	2.587514
C ₄ H ₆	4.49599		

Table 8. The $\vec{IP}_{tr}$ value of each substances in naphtha (2).

Substance	IP_j Value (%)	C_{4+}	4.86766
H ₂	9.056091	C ₂ H ₂	2.530207
CH ₄	14.6854	C _n H _{2n-6}	3.339963
C ₂ H ₄	19.70367	I-C ₄ H ₈	5.933869
C ₂ H ₆	4.47801	N-C ₄ H ₁₀	2.598407
C ₃ H ₆	8.586633	B	2.887175
C ₃ H ₈	2.719097	T	2.54081
C ₄ H ₁₀	2.617593	EB	2.573647
C ₄ H ₈	3.757652	ST	2.579013
C ₄ H ₆	4.545106		

The importance of substances in the reaction network shows that the ethylene importance of these two naphtha is higher than that of all substances, and the importance of propylene is higher than that of all substances with a carbon atom number of 3, which is consistent with the experience in actual production whereby ethylene and propylene are the two most important products. At the same time, the biggest difference between the two materials is C_{4+} , which is the weakness of Kumar model.

After calculating the importance of each substance, for each S_p s, the $IV_{SP=k}$ can be summarized as Formula (16). The result is presented in Figure 6. The approach is illustrated in Section 3.1.

Figure 6. The $IV_{SP=k}$ value of different S_p .

From Figure 6 and Tables 7 and 8, we can see the scope of $S_p \geq 3$ has covered the major part of the Kumar model with the criterion listed in Formula (17). (As the result of our experience the threshold value TV is set as 80%). So, the minimal scope is $S_p \geq 3$. ($3 \leq S_p \leq 4$) to ensure that the important (ethylene, propylene) and primary reactions are enhanced.

4.3. Parameter Optimization on the Basis of MRE Analysis

When trying to find optimal S_p value, experiments of different S_p values are carried out and assessed with MRE value. MREs for each S_p value are calculated with the Formula (18) and the results are presented in Figure 7.

From Figure 7 we can see, the K-R model with $S_p = 3$ performs the best. For naphtha (1), the error of ethylene and propylene get larger appreciably when S_p changes from 3 to 4, but the error of the other product has a dramatic increase when S_p changes from 3 to 4. For naphtha (2), although the error of products in $S_p = 3$ and $S_p = 4$ are nearly the same, the error of ethylene and propylene get large rapidly which is unacceptable in ethylene industry. The reason why naphthas (1) and (2) are chosen is that during the research of Kumar model, we found that naphthas (1) and (2) are two typical feedstocks. For both of them, the optimal S_p value is 3.

When the optimal S_p value is determined, the structure of K-R model is fixed. Modeling of two naphtha cracked in SL-1 furnace compared with the original Kumar model are presented in Tables 6 and 9.

The results from Tables 9 and 10 present that the performance of K-R model is better regarding different kinds of naphtha decomposition. Further, the computation time is 11.392 s (K-R) to 2.351 s (Kumar) which are acceptable.

Figure 7. MRE of the K-R model in conditions of different Sp.

Table 9. Compared Result between the Kumar and K-R models with naphtha (1).

Substance	Target Yields (wt %)	Kumar Yields (wt %)	Relative Errors 1 (%)	K-R Model Yields (wt %)	Relative Errors 2 (%)
H ₂	1.09	1.2776	17.211	0.8733	−19.880733
CH ₄	16.85	12.86	−23.6795	13.0195	−22.7329
C ₂ H ₄	28.83	27.386	−5.00867	28.5798	−0.86785
C ₂ H ₆	2.86	2.006	−29.8601	3.56	24.4755
C ₃ H ₆	13	17.163	32.02307	15.7391	21.07
C ₄ H ₈	3.43	3.4139	−0.4694	3.55	3.49854
C ₄ H ₆	4.64	3.3741	−27.2823	3.72	−19.8276
MRE (%)			22.49		18.36

Table 10. Compared Result between the Kumar and K-R models with naphtha (4).

Substance	Target Yields (wt %)	Kumar Yields (wt %)	Relative Errors 1 (%)	K-R Model Yields (wt %)	Relative Errors 2 (%)
H ₂	1.06	1.2567	18.5566	0.8532	−19.5094
CH ₄	16.57	12.656	−23.621	12.8766	−22.2897
C ₂ H ₄	30.22	26.952	−10.814	30.0053	−0.71046
C ₂ H ₆	3.08	1.9732	−35.9351	3.7749	22.56169
C ₃ H ₆	13.61	16.877	24.00441	16.6434	22.28802
C ₄ H ₈	3.48	3.3509	−3.70977	3.5067	0.767241
C ₄ H ₆	4.76	3.3244	−30.1597	3.6635	−23.0357
MRE (%)			23.33		18.57

4.4. Parameter Optimization of $\vec{I}_s$ Value

While optimizing the first-order reaction, the contrast experiments between the formal Kumar model with error correction chaos optimization method and K-R model with SQP method is done. The result of naphtha (1) is showed in Table 11. The result of naphthas (2) and (3) are also similar.

Table 11. The optimization result of naphtha (1).

Substance	Target Yields (wt %)	Kumar Yields (wt %)	Relative Errors 1 (%)	Optimized K-R Model Yields (wt %)	Relative Errors 2 (%)
H ₂	1.09	1.091	0.091743	1.0903	0.027523
CH ₄	16.85	16.854	0.023739	16.8625	0.074184
C ₂ H ₄	28.83	28.837	0.024280	28.8375	0.026015
C ₂ H ₆	2.86	2.8602	0.006993	2.861	0.034965
C ₃ H ₆	13	13.002	0.015385	13.0024	0.018462
C ₄ H ₈	3.43	3.4285	−0.043732	3.4321	0.061224
C ₄ H ₆	4.64	4.6399	−0.002155	4.6385	−0.03233
MRE (%)			0.04		0.04

Naphtha (4)–(9) can't obtain the reasonable solution. However, with the help of the K-R model with SQP method, accurate result can be derived and an example of naphtha (4) is presented in Table 12. Data on naphthas (4)–(9) can be found in our previous work [21].

Table 12. The optimization result of naphtha (4).

Substance	Target Yields (wt %)	Kumar Yields (wt %)	Relative Errors 1 (%)	Optimized K-R Model Yields (wt %)	Relative Errors 2 (%)
H ₂	1.06	1.2567	0.996241	1.0595	−0.04717
CH ₄	16.57	12.656	16.93835	16.5834	0.080869
C ₂ H ₄	30.22	26.952	30.97339	30.2132	−0.0225
C ₂ H ₆	3.08	1.9732	3.267048	3.0814	0.045455
C ₃ H ₆	13.61	16.877	14.40224	13.6173	0.053637
C ₄ H ₈	3.48	3.3509	3.782969	3.4765	−0.10057
C ₄ H ₆	4.76	3.3244	5.025989	4.7621	0.044118
MRE (%)			5.67		0.061

The initial $\vec{I}_s$ value is showed in Table 13.

Table 13. The initial $\vec{I}_s$ value of naphthas (1) and (4).

Naphtha (1)	I_s Value	Naphtha (4)	I_s Value
1. H ₂	0.4682	1. H ₂	0.4469
2. CH ₄	0.9799	2. CH ₄	0.9883
3. C ₂ H ₄	0.9783	3. C ₂ H ₄	1.0333
4. C ₂ H ₆	0.1450	4. C ₂ H ₆	0.1571
5. C ₃ H ₆	0.4602	5. C ₃ H ₆	0.4926
6. C ₃ H ₈	0.0089	6. C ₃ H ₈	0.0098
7. C ₄ H ₁₀	0.0144	7. C ₄ H ₁₀	0.0137
8. C ₄ H ₈	0.1998	8. C ₄ H ₈	0.2008
9. C ₄ H ₆	0.1072	9. C ₄ H ₆	0.1123
10. C ₄ ⁺	0.1932	10. C ₄ ⁺	0.1605

From Table 11, we can see the MRE of the first naphtha is nearly the same in the two ways, but when refer to the second kind of naphtha in Table 12, the Kumar model can't provide an accurate

solution. The errors of ethylene and propylene are too large for industrial application, but the K-R model put up a good performance. This means the K-R model has a wider adaptive range of raw materials while optimizing. This is because the K-R model has enriched its important reactions with free-radical approach which is more suitable in describing the cracking.

4.5. Result Discussions

- (1). In the PR calculation, the parameter ε will influence the result. When α becomes large, all important (IP_j values) tend to average. When a small value is assigned to α , the result will consider more about resultant. For the case study, $\alpha = 0.0005$ is adopted.
- (2). While performed PR calculation in conditions of different feedstock, the $\vec{IP}_j$ value of each substance may be different, but the summarized results of each S_p value are nearly the same. Results of $S_p = 3$ and $S_p = 4$ are all over 80%. This proved that the algorithm demonstrates robustness. At the same time, the difference in the calculation results between the two naphtha is mainly found in C4+, which is where Kumar's equation ignores. The following different modeling results confirm the necessity of enhancing this part of the reaction and the correctness of the method.
- (3). In the simulation of naphtha, the optimal S_p value is 3. Experiments for both of the two typical feedstock indicates that if we let $S_p = 4$, the error of product yield will grow rapidly. The reason is that the structure of the Kumar model considers part of the reactions into the first-order reactions.
- (4). During the case study, we find that there are two kinds of naphtha. They performance totally different when modeling:
- (5). For the first kind of naphtha, like feedstocks (1), (2), and (3), both the K-R model and Kumar model can reach the accuracy of 0.06%, but the K-R model converges faster. The convergence rate of the K-R optimal modeling and Kumar optimal modeling are 35 min and 20 h respectively.
- (6). For the second kind of naphtha, like feedstocks (4)–(9), the Kumar model can't get the reasonable result. Errors in ethylene (31%) and propylene (14%) are too large to accept. On the contrary, the K-R model still performs well. This difference is mainly due to the presence of isomeric reactants, and the lack of a description of such reactions is one of the weaknesses of Kumar's model.
- (7). The K-R model relative errors are often very different from the Kumar relative errors (they also change from positive to negative and vice versa). This phenomenon is due to the equilibrium constraint between carbon and hydrogen.

The different performances can be explain by the theory of co-pyrolysis. Zhang Lijun [33] in 2011 described these kinds of phenomena between n-butane and i-butane and found that in the mixture of feedstock, if the i-butane gets more, the product yield of propylene will get larger and the one of ethylene will get smaller. The banishing of ethyl can be described by free-radical reactions, but can't be described by molecular dynamics as the secondary reactions in the Kumar model. At the same time, parameter optimization also helps the model to better solve the problem of indeterminate content of isomers in modeling.

From Table 13, we find the error is mainly in propylene, ethylene, and propylene (error > 10%). The product yield of ethylene is undersized and that of propylene is oversized. This is the same with the phenomenon in Zhang's experiment. In this way, the conclusion can be derived that the reason for the different performance of the two models is that, in these feedstocks, the amount of i-butane is greater.

5. Conclusions

A series of K-R models have been developed based on the Kumar model and enriched by free-radicals. In the process of modeling, the suitable model can be selected according to the characteristics of raw materials. While determining the scope of enriched reactions, the improved PR algorithm and MRE analysis are introduced. The algorithm can also be employed as a tool for other reaction analyses. The K-R model is a reliable model which has good adaptability with feedstock.

It solved the problem of feedstock adaptability and improved the accuracy of the Kumar model. Further, it avoids reconstruction in the free-radical approach which is difficult and causes errors.

In future, the application of the K-R model in other raw material needs to be verified. Relevant sensitivity analysis experiments are also necessary. Due to the free-radical network, light feedstock like propane is supposed to fit the model, and the naphtha has been tested by experiments, but other raw materials, like HVGO, need more verification.

6. Statement of Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Author Contributions: In this paper, the experimental work and thesis writing were mainly undertaken by P.M., while X.G. was mainly responsible for the review, guidance and revision of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Nomenclature

C_{4+}	Hydrocarbons containing more than four carbon atoms per molecule
E	The activation energy of the reaction
k_0	The rate constant of the reaction
B	Benzene
T	Toluene
EB	Ethyl benzene
$i-C_4H_8$	Isobutene
S_p	Structural parameters of K-R model
MRE	Mean relative error
C_j	Mass fraction of substance j
S_j	Substance j
R_r	Reaction r
T_m	The temperature at any given moment in the tube of cracking furnace
P_m	The pressure at any given moment in the tube of cracking furnace
M_m	The Transfer matrix for T_m and P_m
$M_{r,m}$	The component of M_m calculated by reaction r
$k_{r,m}$	The rate of reaction r calculated by Arrhenius equation under T_m and P_m
tr	Reaction termination
$\vec{IP}_m$	Material importance vector (iteration quantity) calculated by IPR algorithm
ϵ	The shift factor in IPR
N	Number of species
Δt	Iteration time per step
$IV_{Sp=k}$	The calculation result of material importance when $Sp = k$
TV	Threshold value

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