

## **Supporting Information for Mathematical Modeling of the Catalytic Pyrolysis of High Density Polyethylene in a Plug-Flow Tubular Reactor**

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### **Summary of discussion on type of catalysts used in plastics pyrolysis**

The catalysts employed in these processes are solid materials containing acid sites. The first catalysts employed for the pyrolysis of plastics were amorphous oxides with acid sites, such as alumina, silica-alumina, and others (31), as well as clays (32).

The poor acid strength of these amorphous materials, as well as their lack of an ordered structure that could allow the control of the product selectivity, led to the development of new types of catalysts with greater activity and selectivity. Zeolites have become the most used type of catalysts in this field due to their high acidity and shape selectivity. (33) The initial investigations of these materials are related to catalysts used in refinery processes (34), such as zeolites Y, X, ZSM-5 or mordenite (35). Due to the relatively large dimensions of the plastic macromolecules, their diffusion through the zeolite micropores is hindered (pore diameter  $< 12 \text{ \AA}$ ), so only active centers located on the external surface of the catalyst can be reached by them, limiting the activity of the catalyst. To minimize this problem, meso-structured materials (MCM-41 o SBA-15) that contain an ordered array of mesoporous channels have been developed. (36) These materials lead to high conversions and yields of liquid hydrocarbons, with lower production of gases, due to their lower acidity and larger pore size, between 2.5 and 30 nm. Besides, they show lower selectivities towards aromatic compounds and higher yields of isoparaffins and olefins. Their main drawback is their moderate acidity as their walls do not exhibit a crystalline structure. (37) More recent approaches include the use of zeolites with nanometric-size crystals (and therefore large

external surface) exhibiting higher activities in plastics degradation, (38) as well as hierarchically porosity zeolites, that incorporate mesopores in their original microporous structure. (39)

#### Figures showing results of isobutane cracking simulations

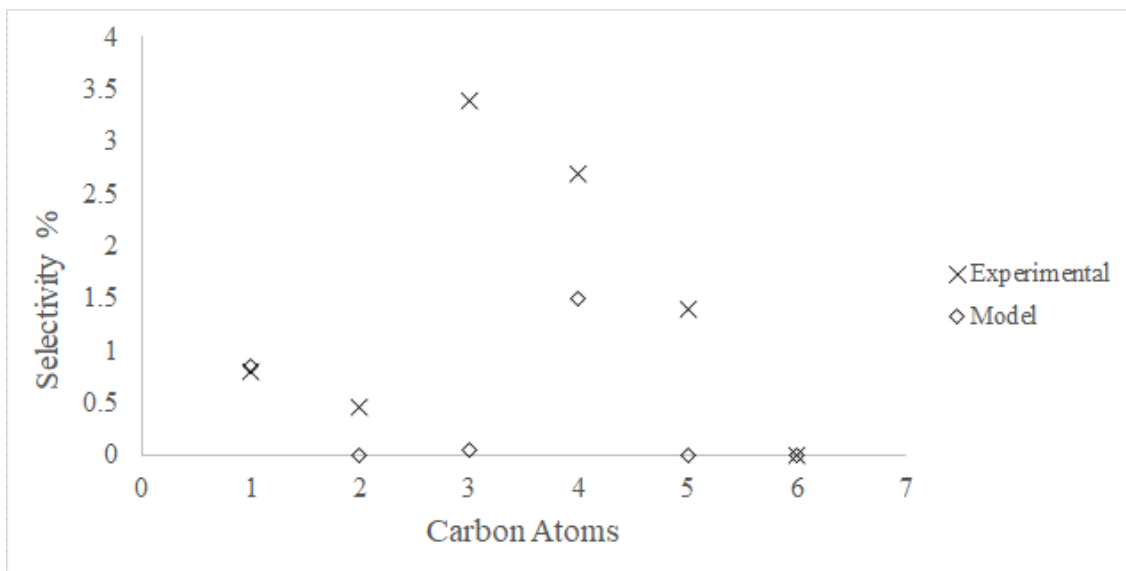


Figure 12 S1. Selectivity of the paraffinic products in the catalytic pyrolysis of *iso*-butane with USY type zeolite catalyst at 550 °C.

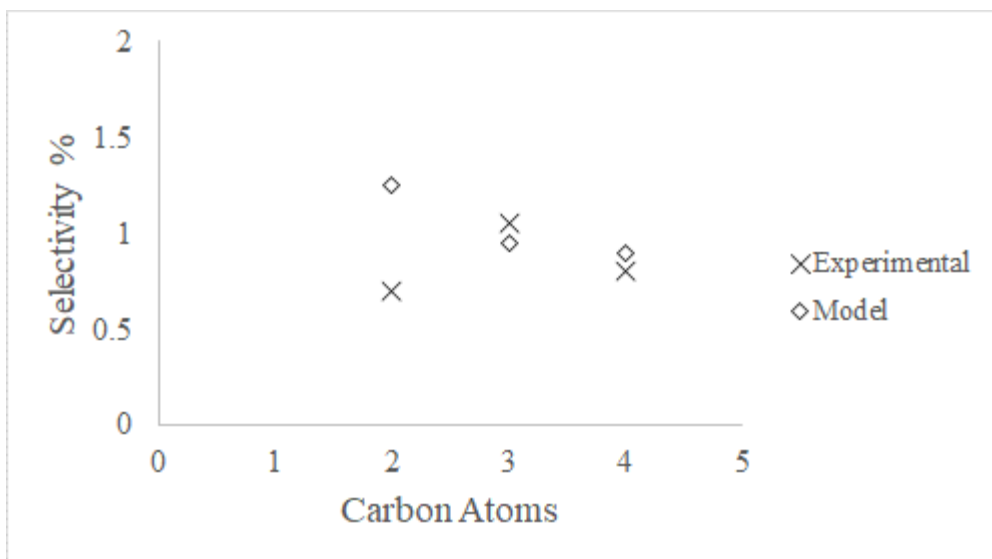


Figure S2. Selectivity of the olefinic products in the catalytic pyrolysis of *iso*-butane with USY type zeolite catalyst at 550 °C.

## Kinetic parameters used in the simulations

Table S1. Values of kinetic parameters in Arrhenius form  $k = A \exp\left(\frac{E_a}{RT}\right)$  used in simulations. Units for pre-exponential factors are  $\text{s}^{-1}$  for first order reactions and  $\text{Lmol}^{-1}\text{s}^{-1}$  for second order reactions, and  $\text{kcal/mol}$  for activation energies. All parameter values taken from (26) except where indicated.

Kinetic constant	$\log_e A$	$E_a$	Case <sup>1</sup>
$k_{d_1}$	4.3	20.1	1,2,3,4
$k_{d_1}^-$	14.4	47.3	1,2,3,4
$k_{d_2}$	4.4	18.2	1,2,3,4
$k_{d_2}^-$	14.2	37.1	1,2,3,4
$k_{i_{p1}}$	20.1	40.1	1,2,3,4
$k_{i_{p2}}$	20.2	39.1	1,2,3,4
$k_{i_o}$	18.1	27.1	1,2,3,4
$k_{p_1}$	20.7	23.3	2,3,4
$k_{p_1}$	11.6 <sup>2</sup>	16.7 <sup>2</sup>	1
$k_\beta$	18.1	27.1	1,2,3,4
$k_{des}$	14.4	47.3	1,2,3,4

<sup>1</sup>Cases simulated: 1) isobutane, 2) n-heptane, 3) HDPE-1, 4) HDPE-2.

<sup>2</sup>Taken from reference (53).

## Evolution of the paraffin distribution $P_n$ at different z positions

Figures S3 to S5 show the evolution of the normalized distribution of paraffins,  $P_n$ , at different positions  $z$  along the reactor (total length of 30.5 cm), for the simulation of the HDPE1 case (mainly waxes) having an Si/Al ratio of 30 and two different types of initial

conditions: A) the total weight for a fraction is assigned to chains with the average length in that fraction; B) the total weight for a fraction is distributed along each individual length in the fraction, so as to the number distribution in that fraction is uniform. In both cases the number average molecular weight  $M_n$  is the same. The plots show that the shape of the distribution smooths out with the progress of the reaction, and it spreads out to both ends, increasing the relative contributions of long and short chains. In case A the peaks of the original distribution are gradually consumed, while in case B the sharp steps of the original distribution are smoothed out. In general, the mode of the distribution shifts towards shorter chains, and the relative contribution of the C1-C4 fraction becomes relevant, even at short values of  $z$ .

Notably, the final shape of the distribution for cases A and B is essentially the same, in spite of the differences in the distributions fed as initial conditions.

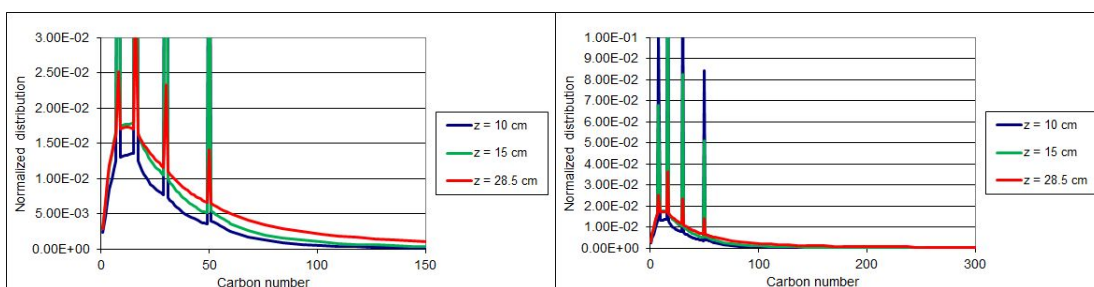


Figure S3. Evolution of the normalized number distribution of paraffins (simulation), for the catalytic pyrolysis of HDPE waxes using a HZSM-5 zeolite catalyst at 500 °C, Si/Al ratio of 30 for initial conditions A (see text). Left plot is a zoom at the region of short carbon numbers.

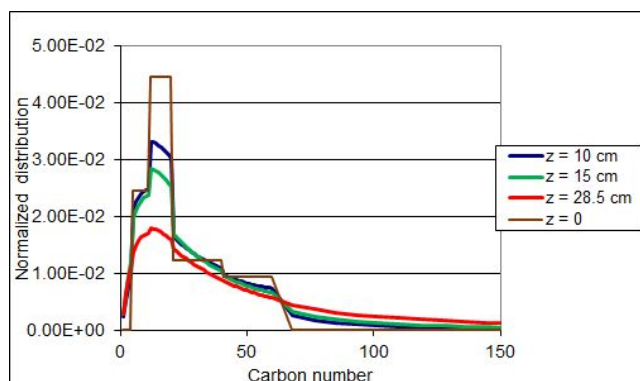


Figure S4. Evolution of the normalized number distribution of paraffins (simulation), for the catalytic pyrolysis of HDPE waxes using a HZSM-5 zeolite catalyst at 500 °C, Si/Al ratio of 30 for initial conditions B (see text).

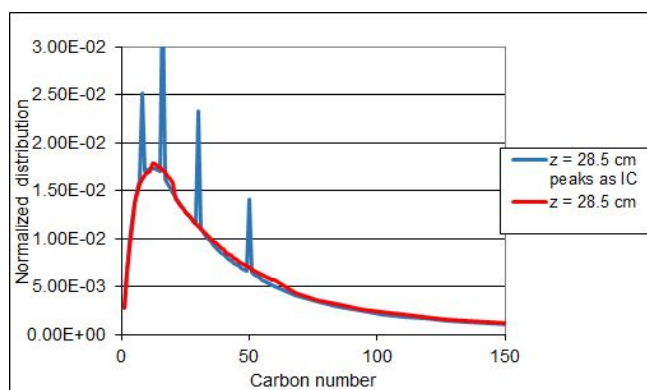


Figure S5. Comparison of final normalized number distributions of paraffins (simulation), for the catalytic pyrolysis of HDPE waxes using a HZSM-5 zeolite catalyst at 500 °C, Si/Al ratio of 30 for initial conditions (IC) A and B (see text).