Supplementary data for

Intensification of Ethylene Production from Naphtha via a Redox Oxy-Cracking Scheme: Process Simulations and Analysis

Vasudev Pralhad Haribal [a], Yun Chen [a,b], Luke Neal [a], Fanxing Li [a,*]

[a] *Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695–7905, USA*
[b] *School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China*

* Corresponding author.
E-mail address: fli5@ncsu.edu (F. Li)

1. The ASPEN Plus® process configuration

The ASPEN Plus® simulation model for naphtha (or hexane) steam cracking is shown in Fig. S1. The upstream and downstream sections have been highlighted and so are the reactor and the compressor. The downstream consists of the quench system, the primary fractionation, the compressor, the refrigeration unit (cold box), the pressure swing adsorption (PSA) unit, and the separation columns. The different columns have been identified in the figure. The pre-heated naphtha (or hexane) feed and steam can be seen as the inlet streams to the reactor. The reactor is operated at 775 ℃. For simplicity, a single-pass is considered here. The major products leaving the system include ethylene and propylene from the C2 and C3 splitter, respectively.

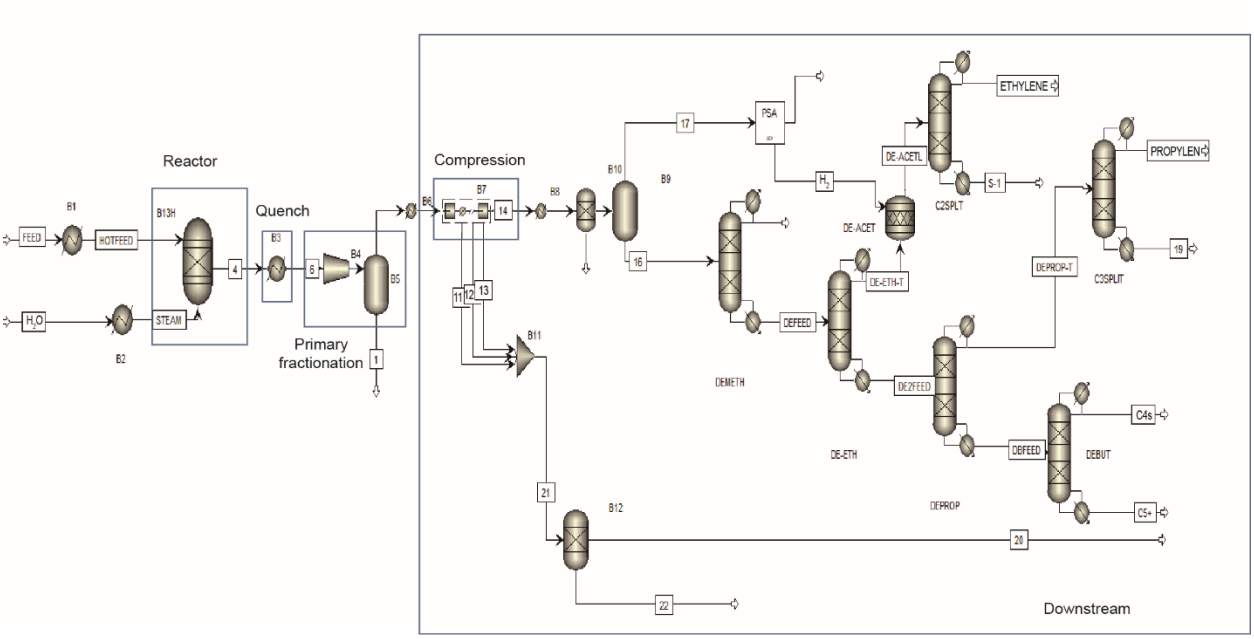

Fig. S1. ASPEN Plus® flowsheet for hexane cracking. PSA: pressure swing adsorption.

The simulation model for the redox oxy-cracking (ROC) process is shown in Fig. S2. The downstream section is identical to the cracking process. The cracking reactor has been replaced by the chemical looping reactors, which include the ROC reactor and the regenerator. Pre-heated hexane is fed to the ROC reactor which operates at 775 ℃. The feed to the regenerator includes the reduced catalyst from the ROC reactor (reducer) and pre-heated air. The oxidized catalyst from the regenerator, at 935 ℃, has been recycled to the ROC reactor as depicted in Fig. S2.

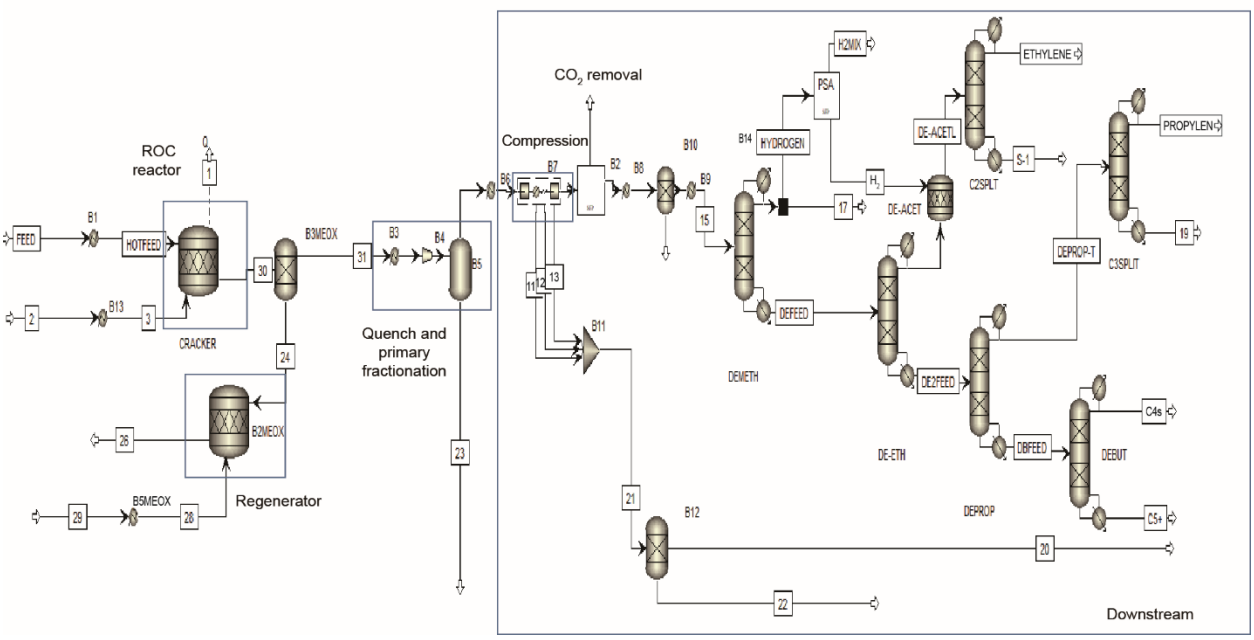

Fig. S2. ASPEN Plus® flowsheet for the ROC process.

2. High ROC case

The following Table S1 shows the product distribution used for the ROC high conversion case.

Table S1
Product distributions for ROC high conversion case.

Component	%C yield
Hydrogen	0.0
Methane	9.6
Acetylene	0.6
Ethylene	35.6
Ethane	2.8
Propadiene	0.7
Propylene	13.0
Propane	0.2
C4s	0.0
Butadiene	3.4
Butene	2.5
Butane	0.1
Benzene	14.2
Toluene	0.0
Xylene	0.0
Ethyl benzene	8.7
Styrene	0.0
Naphthalene	0.0
n-pentane	1.6

n-hexane	2.4
iso-heptane	0.0
iso-octane	0.0
Cyclohexane	0.0
TMB	0.0
Dodecane	0.0
CO	1.3
CO_2	3.4

TMB: tetramethylbenzidine.

3. Deacetylenizer conditions

Table S2 provides the conditions used for the deacetylenizer, based on an industrial cracking unit. For the deacetylenizer, negligible conversion of ethylene to ethane has been assumed [2].

Table S2
Deacetylenizer conditions.

Parameters	Settings
Pressure	25 atm (1 atm = 1.013×10^5 Pa)
Feed H_2/C_2H_2 ratio	1:1
Feed CO concentration	5–60 mg L^{-1} (Higher in the ODH case)
Temperature	50–70 °C
Feed C_2H_2 concentration	< 0.8 vol%
C_2H_2 to C_2H_4 conversion	80%

ODH: oxidative dehydrogenation.

4. Process material flow

Table S3 and Table S4 show the molar flow rate of the components in various streams in the process for the cracking process and the ROC process, respectively. The results have been exported from the corresponding Aspen Plus® simulations.

Table S3
Material flow in the cracking process (unit: kmol h^{-1}).

	Feed	Outlet	DM top	DE top	DP top	C2-split top	C3-split top	DB top
Hydrogen	0	327.6	16.9	0	0	1.4	0	0
Methane	0	287.5	218.3	0.2	0	0.2	0	0
Acetylene	0	8.3	0	7.9	0	1.2	0	0
Ethylene	0	409.1	2.0	391.4	0	397.7	0	0
Ethane	0	41.5	0	39.8	0.2	0	0.2	0
Propadiene	0	6.8	0	0	6.0	0	0	0
Propylene	0	102.9	0	0	93.9	0	93.5	0
Propane	0	2.5	0	0	2.3	0	0	0
Vinyl acetylene	0	1.2	0	0	0	0	0	0
Butadiene	0	25.7	0	0	0	0	0	0
Butene	0	17.6	0	0	0.2	0	0	1.5
Butane	0	0.9	0	0	0	0	0	0.7
Benzene	0	55.9	0	0	0	0	0	0
Toluene	0	9.2	0	0	0	0	0	0

Xylene	0	3.3	0	0	0	0	0	0
Ethyl benzene	0	1.3	0	0	0	0	0	0
Styrene	0	4.1	0	0	0	0	0	0
Dodecane	0	7.5	0	0	0	0	0	0
n-pentane	0	9.9	0	0	0	0	0	0
n-hexane	500	90.0	0	0	0	0	0	0
iso-heptane	0	7.1	0	0	0	0	0	0
iso-octane	0	3.1	0	0	0	0	0	0
Cyclohexane	0	4.3	0	0	0	0	0	0
TMB	0	3.0	0	0	0	0	0	0
Dodecane	0	0.0	0	0	0	0	0	0

DM: demethanizer; DE: deethanizer; DP: depropanizer; DB: debutanizer.

Table S4
Material flow in the ROC process (unit: kmol h^{-1}).

	Feed	Outlet	DM top	DE top	C2-split top	DP top	C3-split top	DB top
Methane	0.0	229.8	211.9	0.2	0.2	0.0	0.0	0.0
Ethane	0.0	30.9	0.0	29.6	0.0	0.1	0.1	0.0
Ethylene	0.0	479.3	2.2	464.9	467.2	0.0	0.0	0.0
Propane	0.0	5.7	0.0	0.0	0.0	5.1	0.0	0.0
Propylene	0.0	162.4	0.0	0.0	0.0	146.7	146.1	0.0
iso-butane	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1
n-butane	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.5
Propadiene	0.0	0.2	0.0	0.0	0.0	0.2	0.0	0.0
Acetylene	0.0	4.4	0.0	4.2	0.0	0.0	0.0	0.0
trans-2-butene	0.0	2.3	0.0	0.0	0.0	0.0	0.0	1.5
1-butene	0.0	51.8	0.0	0.0	0.0	0.0	0.0	37.8
iso-butylene	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.4
CO_2	0.0	39.9	0.0	0.0	0.0	0.0	0.0	0.0
cis-2-butene	0.0	1.9	0.0	0.0	0.0	0.0	0.0	1.2
2-methyl-butane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n-pentane	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
1,3-butadiene	0.0	30.4	0.0	0.0	0.0	0.0	0.0	21.8
Methyl-acetylene	0.0	0.7	0.0	0.0	0.0	0.6	0.0	0.0
trans-2-pentene	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.1
2-methyl-2-butene	0.0	5.6	0.0	0.0	0.0	0.0	0.0	0.2
1-pentene	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.1
cis-2-pentene	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	39.9	37.0	0.0	0.0	0.0	0.0	0.0
n-hexane	500.0	117.1	0.0	0.0	0.0	0.0	0.0	0.0
Benzene	0.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0
Ethylvenzene	0.0	6.9	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen	0.0	40.3	37.4	0.0	0.0	0.0	0.0	0.0
Water	0.0	214.1	0.0	0.0	0.0	0.0	0.0	0.0

References

[1] Zimmermann H, Walzl R. Ethylene. In: Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH; 2000.

[2] Battiston GC, Dalloro L, Tauszik GR. Performance and aging of catalysts for the selective hydrogenation of acetylene: a micropilot-plant study. Appl Catal 1982;2(1):1–17.