Supplementary Information for

"*Comparative life cycle assessment of transportation fuels via co-processing of bio-oil and vacuum gas oil in an existing refinery*"

Meirong Shi [a], Le Wu [b,*], Kun Qian [c], Furong Hong [c]

a School of Pharmacy, Shannxi Institute of International Trade & Commerce, Xi'an 712046, China

b School of Chemical Engineering, Northwest University, Xi'an 710069, China

c CNOOC Ningbo Daxie Petrochemical Ltd., Ningbo 315812, China

*Corresponding Author

Tel: +86-29-88302632

E-mail: lewu@nwu.edu.cn

1. Material Balance

According to our previous work[1] and other studies [2, 3], several assumptions have proposed:

1. The ash is ignored in the model.
2. A linear relationship is assumed between the flow rate of feed streams, and heat and power consumptions of the bio-refinery units.
3. The split fractions of species for non-reacting processes and product distributions of the reacting units of the hydrocarbon bio-refinery are retrieved from modeling results of similar processes.
4. The slight difference in the composition of gasoline and diesel produced by different scenarios is neglected.

1.1 Material balance

1.1.1 Biomass pyrolysis

The material balance of each equipment in biomass fast pyrolysis and catalytic pyrolysis is described in eqs(1)~(24). These equations are derived from references[4].

Grinder:

$$m_i^{\mathrm{pgrd,bms,in}} = m_i^{\mathrm{pgrd,bms,out}} \tag{1}$$

where $m_i^{\mathrm{pgrd,bms,in}}$ is the biomass flowrate of the grinder inlet in the pyrolysis process, in $t \cdot h^{-1}$. The superscripts pgrd, bms, in and out denote the grinder in pyrolysis process, biomass, inlet and outlet streams, respectively. The subscript *i* is the set of the bio-oil production processes i.e. fast pyrolysis or catalytic pyrolysis.

Drier:

$$m_i^{\mathrm{pgrd,bms,out}} = m_i^{\mathrm{pdry,bms,in}} \tag{2}$$

$$m_i^{\mathrm{pdry,bms,in}} + m_i^{\mathrm{pdry,bg,in}} = m_i^{\mathrm{pdry,bms,out}} + m_i^{\mathrm{pdry,exh,out}} \tag{3}$$

where $m_i^{\mathrm{pdry,bms,in}}$ and $m_i^{\mathrm{pdry,bms,out}}$ represent the biomass flowrates of the inlet and outlet streams of the drier, in t·h^{-1}. The superscripts pdry, bg and exh denote the drier in pyrolysis process, bio-gas and exhaust gas of the drier, respectively.

Convertor:

$$m_i^{\text{pdry,bms,out}} = m_i^{\text{pcvt,bms,in}} \tag{4}$$

$$m_i^{\text{pcvt,bms,out}} = m_i^{\text{pcvt,bms,in}} \tag{5}$$

where $m_i^{\text{pcvt,bms,out}}$ and $m_i^{\text{pcvt,bms,in}}$ are the biomass flowrates of the inlet and outlet streams of the convertor, in t·h^{-1}. The superscript pcvt denotes the convertor in pyrolysis process.

Pyrolysis reactor:

$$m_i^{\text{pcvt,bms,out}} = m_i^{\text{ppyr,bms,in}} \tag{6}$$

$$m_i^{\text{ppyr,bms,in}} + m_i^{\text{ppyr,sand,in}} = m_i^{\text{ppyr,bo,out}} + m_i^{\text{ppyr,bg,out}} + m_i^{\text{ppyr,bc,out}} + m_i^{\text{ppyr,sand,out}} \tag{7}$$

$$m_i^{\text{ppyr,sand,in}} = m_i^{\text{ppyr,sand,out}} \tag{8}$$

$$m_i^{\text{ppyr,bo,out}} = m_i^{\text{ppyr,bms,in}} y_i^{\text{ppyr,bo,out}} \tag{9}$$

$$m_i^{\text{ppyr,bg,out}} = m_i^{\text{ppyr,bms,in}} y_i^{\text{ppyr,bg,out}} \tag{10}$$

$$m_i^{\text{ppyr,bc,out}} = m_i^{\text{ppyr,bms,in}} y_i^{\text{ppyr,bc,out}} \tag{11}$$

where $m_i^{\text{ppyr,bms,in}}$ and $m_i^{\text{ppyr,sand,in}}$ represent the biomass and sand flowrates of the inlet streams of the pyrolysis reactor, in t·h^{-1}. The superscripts ppyr, sand, bo, bg and bc denote the pyrolysis reactor in pyrolysis process, sand, bio-oil, bio-gas and bio-char, respectively. $y_i^{\text{ppyr,bo,out}}$ is the bio-oil yield of the pyrolysis reactor, in %. The yields of the fast pyrolysis and catalytic pyrolysis are derived from the references [5-9].

Cyclone:

$$m_i^{\text{ppyr,bo,out}} + m_i^{\text{ppyr,bg,out}} + m_i^{\text{ppyr,bc,out}} + m_i^{\text{ppyr,sand,out}} = m_i^{\text{pcyl,in}} \tag{12}$$

$$m_i^{\text{pcyl,in}} = m_i^{\text{pcyl,out,top}} + m_i^{\text{pcyl,out,bot}} \tag{13}$$

$$m_i^{\text{pcyl,out,top}} = m_i^{\text{ppyr,bo,out}} + m_i^{\text{ppyr,bg,out}} \tag{14}$$

$$m_i^{\text{pcyl,out,bot}} = m_i^{\text{ppyr,bc,out}} + m_i^{\text{ppyr,sand,out}} \tag{15}$$

where $m_i^{\text{pcyl,in}}$ is the mass flowrate of the inlet stream of cyclone in pyrolysis process, in t·h^{-1}. The superscripts pcyl, top and bot denote the cyclone in pyrolysis process, top and bottom streams, respectively.

Furnace:

$$m_i^{\text{pfur,in}} = m_i^{\text{pcyl,out,bot}} \tag{16}$$

$$m_i^{\text{pfur,in}} + m_i^{\text{pfur,air,in}} + m_i^{\text{pfur,bg,in}} = m_i^{\text{pfur,sand,out}} + m_i^{\text{pfur,exh,out}} \tag{17}$$

$$m_i^{\text{pfur,sand,out}} = m_i^{\text{ppyr,sand,in}} \tag{18}$$

where $m_i^{\text{pfur,in}}$ is the mass flowrate of the inlet stream of furnace in pyrolysis process, in t·h^{-1}. The superscripts pfur and air denote the furnace in pyrolysis process and air blowing to the furnace, respectively.

Quench:

$$m_i^{\text{pqnc,in}} = m_i^{\text{pcyl,out,top}} \tag{19}$$

$$m_i^{\text{pqnc,in}} = m_i^{\text{pqnc,bo,out}} + m_i^{\text{pqnc,bg,out}} \tag{20}$$

$$m_i^{\text{pqnc,bo,out}} = m_i^{\text{pqnc,in}} y_i^{\text{pqnc,bo,out}} \tag{21}$$

$$m_i^{\text{pqnc,bg,out}} = m_i^{\text{pqnc,in}} y_i^{\text{pqnc,bg,out}} \tag{22}$$

where $m_i^{\text{pqnc,in}}$ is the mass flowrate of the inlet stream of quench in pyrolysis process, in t·h^{-1}. The superscript pqnc denotes the quench in pyrolysis process.

Bio-gas splitter:

$$m_i^{\text{psplt,bg,in}} = m_i^{\text{pfur,bg,in}} + m_i^{\text{pdry,bg,in}} + m_i^{\text{py,bg,out}} \tag{23}$$

$$m_i^{\text{psplt,bg,in}} = m_i^{\text{pqnc,bg,out}} \tag{24}$$

where $m_i^{\text{psplt,bg,in}}$ is the mass flowrate of the inlet stream of splitter in pyrolysis process, in t·h^{-1}. The superscript psplt denotes the bio-gas splitter in pyrolysis process.

1.1.2 Fast pyrolysis oil HDT process

In this section, "*i*" only denotes the fast pyrolysis because the fast pyrolysis oil need to be hydrotreated before its co-feeding to an FCC with VGO. According to the previous studies[2, 10], the material balance of this process is shown as follows:

Bio-oil feed pump:

$$m_i^{\mathrm{pqnc,bo,out}} = m_i^{\mathrm{bfp,bo,in}} \tag{25}$$

$$m_i^{\mathrm{bfp,bo,in}} = m_i^{\mathrm{bfp,bo,out}} \tag{26}$$

where $m_i^{\mathrm{bfp,bo,in}}$ and $m_i^{\mathrm{bfp,bo,out}}$ are the bio-oil flowrates from the fast pyrolysis of the inlet and outlet streams of the feed oil pump, in t·h^{-1}. The superscripts bfp and bo denote the feed oil pump in bio-oil HDT process and bio-oil, respectively.

Make-up hydrogen compressor:

$$m_i^{\mathrm{bmhc,H_2,in}} = m_i^{\mathrm{bmhc,H_2,out}} \tag{27}$$

where $m_i^{\mathrm{bmhc,H_2,in}}$ and $m_i^{\mathrm{bmhc,H_2,out}}$ are the hydrogen flowrates of the inlet and outlet streams of the make-up hydrogen compressor, in t·h^{-1}. The superscripts bmhc and H_2 denote the make-up hydrogen compressor in bio-oil HDT process and hydrogen, respectively.

Recycling hydrogen compressor:

$$m_i^{\mathrm{brhc,H_2,in}} = m_i^{\mathrm{brhc,H_2,out}} \tag{28}$$

where $m_i^{\mathrm{brhc,H_2,in}}$ and $m_i^{\mathrm{brhc,H_2,out}}$ are the hydrogen flowrates of the inlet and outlet streams of the recycling hydrogen compressor, in t·h^{-1}. The superscript brhc denotes the recycling hydrogen compressor in bio-oil HDT process.

Furnace:

$$m_i^{\mathrm{bfp,bo,out}} + m_i^{\mathrm{bmh,H_2,out}} + m_i^{\mathrm{brh,H_2,out}} = m_i^{\mathrm{bfur,in}} \tag{29}$$

$$m_i^{\mathrm{bfur,in}} = m_i^{\mathrm{bfur,out}} \tag{30}$$

where $m_i^{\mathrm{bfur,in}}$ and $m_i^{\mathrm{bfur,out}}$ are the flowrates of the inlet and outlet streams of the furnace, in $t \cdot h^{-1}$. The superscript bfur denotes the furnace in bio-oil HDT process.

HDO reactor:

$$m_i^{\text{bfur,out}} = m_i^{\text{brct,in}} \tag{31}$$

$$m_i^{\text{brct,in}} = m_i^{\text{brct,hbo,out}} + m_i^{\text{brct,gas,out}} + m_i^{\text{brct,water,out}} \tag{32}$$

$$m_i^{\text{brct,hbo,out}} = m_i^{\text{brct,in}} y_i^{\text{brct,hbo}} \tag{33}$$

$$m_i^{\text{brct,water,out}} = m_i^{\text{brct,in}} y_i^{\text{brct,water}} \tag{34}$$

$$m_i^{\text{brct,gas,out}} = m_i^{\text{brct,in}} y_i^{\text{brct,gas}} \tag{35}$$

where $m_i^{\text{brct,in}}$ and $m_i^{\text{brct,hbo,out}}$ are the flowrates of the inlet stream and the hydrotreated bio-oil in the HDO reactor, in $t \cdot h^{-1}$. The superscripts brct, hbo, gas and water denote the HDO reactor in bio-oil HDT process, hydrotreated bio-oil, gas and water, respectively. $y_i^{\text{brct,hbo}}$ is the yield of the hydrotreated bio-oil in HDO reactor, in %.

Separator:

$$m_i^{\text{brct,hbo,out}} + m_i^{\text{brct,gas,out}} + m_i^{\text{brct,water,out}} = m_i^{\text{bsep,in}} \tag{36}$$

$$m_i^{\text{bsep,out}} = m_i^{\text{bsep,hbo,out}} + m_i^{\text{bsep,H}_2\text{,out}} + m_i^{\text{bsep,FG,out}} + m_i^{\text{bsep,water,out}} \tag{37}$$

$$m_i^{\text{bsep,hbo,out}} = m_i^{\text{bsep,in}} y_i^{\text{bsep,hbo}} \tag{38}$$

$$m_i^{\text{bsep,H}_2\text{,out}} = m_i^{\text{bsep,in}} y_i^{\text{bsep,H}_2} \tag{39}$$

$$m_i^{\text{bsep,FG,out}} = m_i^{\text{bsep,in}} y_i^{\text{bsep,FG}} \tag{40}$$

$$m_i^{\text{bsep,water,out}} = m_i^{\text{brct,water,out}} \tag{41}$$

where $m_i^{\text{bsep,in}}$ and $m_i^{\text{bsep,out}}$ are the flowrates of the inlet and outlet streams of the HDO separator, in $t \cdot h^{-1}$. The superscripts bsep and FG denote the separator in bio-oil HDT process and fuel gas, respectively.

1.1.3 Bio-oil and VGO co-processing in an FCC

The FCC is considered as a whole and the material balance of the whole FCC, i.e., the input and output streams, is only considered because the FCC is an existing process in the refinery, which can also lower the complexity of the proposed model. The material balance[11] is described as eqs(42)~(48).

$$m_i^{\mathrm{bo}} = m_i^{\mathrm{bsep,hbo,out}} \quad i = \text{fast pyrolysis} \tag{42}$$

$$m_i^{\mathrm{bo}} = m_i^{\mathrm{pqnc,bo,out}} \quad i = \text{catalytic pyrolysis} \tag{43}$$

$$m_i^{\mathrm{VGO}} + m_i^{\mathrm{bo}} = m_i^{\mathrm{FCC,in}} \tag{44}$$

$$m_i^{\mathrm{FCC,out}} = m_i^{\mathrm{FCC,FG,out}} + m_i^{\mathrm{FCC,gs,out}} + m_i^{\mathrm{FCC,ds,out}} + m_i^{\mathrm{FCC,so,out}} \tag{45}$$

$$m_i^{\mathrm{FCC,FG,out}} = m_i^{\mathrm{FCC,in}} y_i^{\mathrm{FCC,FG}} \tag{46}$$

$$m_i^{\mathrm{FCC,gs,out}} = m_i^{\mathrm{FCC,in}} y_i^{\mathrm{FCC,gs}} \tag{47}$$

$$m_i^{\mathrm{FCC,ds,out}} = m_i^{\mathrm{FCC,in}} y_i^{\mathrm{FCC,ds}} \tag{48}$$

$$m_i^{\mathrm{FCC,so,out}} = m_i^{\mathrm{FCC,in}} y_i^{\mathrm{FCC,so}} \tag{49}$$

where m_i^{bo} and m_i^{VGO} are the bio-oil and VGO flowrates before feeding to the FCC, in $\mathrm{t{\cdot}h^{-1}}$; $m_i^{\mathrm{FCC,in}}$ denotes the inlet oil of FCC, in $\mathrm{t{\cdot}h^{-1}}$. The superscripts bo, VGO, FCC, FG, gs, ds and so are bio-oil, vacuum gas oil, FCC, fuel gas, FCC gasoline, FCC diesel and slurry oil, respectively. $y_i^{\mathrm{FCC,FG}}$ denotes the fuel gas yield of FCC, in %.

Beside the material balance of the FCC, the impurities like sulfur, nitrogen, oxygen and aromatics compounds, are also cracked in an FCC and which are then allocated to a certain FCC product based on their boiling points. As the impurity contents in FCC products have strong impacts on the hydrogen consumption of the following HDT units, the impurity distributions of the FCC should be considered. The impurity contents of FCC diesel and FCC gasoline are described in the following equations.

The relations between sulfur contents of the FCC feed oil with the those in FCC diesel and FCC gasoline[11].

$$S_i^{\text{FCC,in}} = \left(m_i^{\text{VGO}} S_i^{\text{VGO}} + m_i^{\text{bo}} S_i^{\text{bo}}\right) \Big/ m_i^{\text{FCC,in}} \tag{50}$$

$$S_i^{\text{FCC,ds,out}} = \text{a}^{\text{S,ds}} S_i^{\text{FCC,in}} + \text{b}^{\text{S,ds}} \tag{51}$$

$$S_i^{\text{FCC,gs,out}} = \text{a}^{\text{S,gs}} S_i^{\text{FCC,in}} + \text{b}^{\text{S,gs}} \tag{52}$$

where $S_i^{\text{FCC,in}}$ is the sulfur content of FCC feed oil, in ppm. a and b denote the calculation coefficients. The superscript S represents the sulfur.

The relations of nitrogen contents are shown in eqs(53)~(55)[11].

$$N_i^{\text{FCC,in}} = \left(m_i^{\text{VGO}} N_i^{\text{VGO}} + m_i^{\text{bo}} N_i^{\text{bo}}\right) \Big/ m_i^{\text{FCC,in}} \tag{53}$$

$$N_i^{\text{FCC,ds,out}} = \text{a}^{\text{N,ds}} N_i^{\text{FCC,in}} + \text{b}^{\text{N,ds}} \tag{54}$$

$$N_i^{\text{FCC,gs,out}} = \text{a}^{\text{N,gs}} N_i^{\text{FCC,in}} + \text{b}^{\text{N,gs}} \tag{55}$$

where $N_{i,j}^{\text{FCC,in}}$ is the nitrogen content of FCC feed oil, in ppm. The superscript N denotes the nitrogen.

The aromatic relations are represented in eqs(56)~(58)[11].

$$A_i^{\text{FCC,in}} = \left(m_i^{\text{VGO}} A_i^{\text{VGO}} + m_i^{\text{bo}} A_i^{\text{bo}}\right) \Big/ m_i^{\text{FCC,in}} \tag{56}$$

$$A_i^{\text{FCC,ds,out}} = \text{a}^{\text{A,ds}} A_i^{\text{FCC,in}} + \text{b}^{\text{A,ds}} \tag{57}$$

$$A_i^{\text{FCC,gs,out}} = \text{a}^{\text{A,gs}} A_i^{\text{FCC,in}} + \text{b}^{\text{A,gs}} \tag{58}$$

where $A_i^{\text{FCC,in}}$ is the aromatics content of FCC feed oil, in %. The superscript A denotes the aromatics.

The relations of oxygen contents are derived from references[12, 13] and shown as eqs(59)~(61).

$$O_i^{\text{FCC,in}} = \left(m_i^{\text{VGO}} O_i^{\text{VGO}} + m_i^{\text{bo}} O_i^{\text{bo}}\right) \Big/ m_i^{\text{FCC,in}} \tag{59}$$

$$O_i^{\text{FCC,ds,out}} = \text{a}^{\text{O,ds}} O_i^{\text{FCC,in}} + \text{b}^{\text{O,ds}} \tag{60}$$

$$O_i^{\text{FCC,gs,out}} = \text{a}^{\text{O,gs}} O_i^{\text{FCC,in}} + \text{b}^{\text{O,gs}} \tag{61}$$

where $O_i^{\text{FCC,in}}$ is the oxygen content of FCC feed oil, in %; $O_i^{\text{FCC,ds,out}}$ and $O_i^{\text{FCC,gs,out}}$

denote the oxygen content of the diesel and gasoline, in ppm. The superscript O represents the oxygen.

1.1.4 FCC diesel HDT process

The material balance[11, 14] of each equipment in the FCC diesel HDT process are shown in eqs(62)~(72).

Feed oil pump:

$$m_i^{\mathrm{FCC,ds,out}} = m_i^{\mathrm{dfp,oil,in}} \tag{62}$$

$$m_i^{\mathrm{dfp,oil,in}} = m_i^{\mathrm{dfp,oil,out}} \tag{63}$$

where $m_i^{\mathrm{dfp,oil,in}}$ and $m_i^{\mathrm{dfp,oil,out}}$ are the feed oil flowrates of the inlet and outlet streams of the feed oil pump, in $\mathrm{t \cdot h^{-1}}$. The superscripts dfp and oil denote the feed oil pump in diesel HDT process and oil, respectively.

Make-up hydrogen compressor:

$$m_i^{\mathrm{dmhc,H_2,in}} = m_i^{\mathrm{dmhc,H_2,out}} \tag{64}$$

where $m_i^{\mathrm{dmhc,H_2,in}}$ and $m_i^{\mathrm{dmhc,H_2,out}}$ are the hydrogen flowrates of the inlet and outlet streams of the make-up hydrogen compressor, in $\mathrm{t \cdot h^{-1}}$. The superscripts dmhc denotes the make-up hydrogen compressor in diesel HDT process.

Recycling hydrogen compressor:

$$m_i^{\mathrm{drhc,H_2,in}} = m_i^{\mathrm{drhc,H_2,out}} \tag{65}$$

where $m_i^{\mathrm{drhc,H_2,in}}$ and $m_i^{\mathrm{drhc,H_2,out}}$ are the hydrogen flowrates of the inlet and outlet streams of the recycling hydrogen compressor, in $\mathrm{t \cdot h^{-1}}$. The superscripts drhc denotes the recycling hydrogen compressor in diesel HDT process.

Furnace

$$m_i^{\mathrm{dfp,oil,out}} + m_i^{\mathrm{dmh,H_2,out}} + m_i^{\mathrm{drh,H_2,out}} = m_i^{\mathrm{dfur,in}} \tag{66}$$

$$m_i^{\mathrm{dfur,in}} = m_i^{\mathrm{dfur,out}} \tag{67}$$

where $m_i^{\mathrm{dfur,in}}$ and $m_i^{\mathrm{dfur,out}}$ are the flowrates of the inlet and outlet streams of the furnace, in $t \cdot h^{-1}$. The superscript dfur denotes the furnace in diesel HDT process.

HDT reactor and separator:

$$m_i^{\text{dfur,out}} = m_i^{\text{drct,in}} \tag{68}$$

$$m_i^{\text{drct,in}} = m_i^{\text{drct,ds,out}} + m_i^{\text{drct,gs,out}} + m_i^{\text{drct,FG,out}} \tag{69}$$

$$m_i^{\text{drct,ds,out}} = m_i^{\text{drct,in}} y_i^{\text{drct,ds}} \tag{70}$$

$$m_i^{\text{drct,gs,out}} = m_i^{\text{drct,in}} y_i^{\text{drct,gs}} \tag{71}$$

$$m_i^{\text{drct,FG,out}} = m_i^{\text{drct,in}} y_i^{\text{drct,FG}} \tag{72}$$

where $m_i^{\text{drct,in}}$ and $m_i^{\text{drct,ds,out}}$ are the flowrates of the inlet stream and the diesel of the HDT reactor and separator, in $t \cdot h^{-1}$. The superscript drct denotes the HDT reactor in diesel HDT process. $y_i^{\text{drct,ds}}$ is the final yield of the diesel in HDT reactor and separator, in %.

1.1.5 FCC gasoline HDT process

Similar to the FCC diesel HDT process, the FCC gasoline and the hydrogen mixture are reacted in the HDT reactor and the reaction effluent is separated to fuel gas and gasoline according to Fig 5. The material balance[11, 14] of each device is represented by eqs(73)~(82).

Feed oil pump:

$$m_i^{\text{FCC,gs,out}} = m_i^{\text{gfp,oil,in}} \tag{73}$$

$$m_i^{\text{gfp,oil,in}} = m_i^{\text{gfp,oil,out}} \tag{74}$$

where $m_i^{\text{gfp,oil,in}}$ and $m_i^{\text{gfp,oil,out}}$ are the feed oil flowrates of the inlet and outlet streams of the feed oil pump, in $t \cdot h^{-1}$. The superscript gfp denotes the feed oil pump in gasoline HDT process.

Make-up hydrogen compressor:

$$m_i^{\text{gmhc},H_2,\text{in}} = m_i^{\text{gmhc},H_2,\text{out}} \tag{75}$$

where $m_i^{\text{gmhc,H}_2\text{,in}}$ and $m_i^{\text{gmhc,H}_2\text{,out}}$ are the hydrogen flowrates of the inlet and outlet streams of the make-up hydrogen compressor, in t·h^{-1}. The superscripts gmhc denotes the make-up hydrogen compressor in gasoline HDT process.

Recycling hydrogen compressor:

$$m_i^{\text{grhc,H}_2\text{,in}} = m_i^{\text{grhc,H}_2\text{,out}} \tag{76}$$

where $m_i^{\text{grhc,H}_2\text{,in}}$ and $m_i^{\text{grhc,H}_2\text{,out}}$ are the hydrogen flowrates of the inlet and outlet streams of the recycling hydrogen compressor, in t·h^{-1}. The superscript grhc denotes the recycling hydrogen compressor in gasoline HDT process.

Furnace:

$$m_i^{\text{gfp,oil,out}} + m_i^{\text{gmh,H}_2\text{,out}} + m_i^{\text{drh,H}_2\text{,out}} = m_i^{\text{gfur,in}} \tag{77}$$

$$m_i^{\text{gfur,in}} = m_i^{\text{gfur,out}} \tag{78}$$

where $m_i^{\text{gfur,in}}$ and $m_i^{\text{gfur,out}}$ are the flowrates of the inlet and outlet streams of the furnace, in t·h^{-1}. The superscript gfur denotes the furnace in gasoline HDT process.

HDT reactor and separator:

$$m_i^{\text{gfur,out}} = m_i^{\text{grct,in}} \tag{79}$$

$$m_i^{\text{grct,in}} = m_i^{\text{grct,gs,out}} + m_i^{\text{grct,FG,out}} \tag{80}$$

$$m_i^{\text{grct,gs,out}} = m_i^{\text{grct,in}} y_i^{\text{grct,gs}} \tag{81}$$

$$m_i^{\text{grct,FG,out}} = m_i^{\text{grct,in}} y_i^{\text{grct,FG}} \tag{82}$$

where $m_i^{\text{grct,in}}$ and $m_i^{\text{grct,gs,out}}$ are the flowrates of the inlet stream and the gasoline of the HDT reactor and separator, in t·h^{-1}. The superscript grct denotes the HDT reactor in gasoline HDT process. $y_i^{\text{grct,gs}}$ is the final yield of the gasoline in HDT reactor and separator, in %.

1.2 Energy balance

The energy balance is the balance between consumption and generation of steam and electricity. The relevant equations are derived from references [2, 3, 10].

1.2.1 Steam and electricity consumptions

The total steam consumption of each process is given by eqs(83)~(87).

$$m_i^{\text{py,steam}} = m_i^{\text{pqnc,bo,out}} f_i^{\text{py,steam}} \tag{83}$$

$$m_i^{\text{bohdt,steam}} = m_i^{\text{bohdt,in}} f^{\text{bohdt,steam}} \tag{84}$$

$$m_i^{\text{FCC,steam}} = m_i^{\text{FCC,in}} f_i^{\text{FCC,steam}} \tag{85}$$

$$m_i^{\text{dhdt,steam}} = m_i^{\text{dfp,oil,in}} f^{\text{dhdt,steam}} \tag{86}$$

$$m_i^{\text{ghdt,steam}} = m_i^{\text{gfp,oil,in}} f^{\text{ghdt,steam}} \tag{87}$$

where $m_i^{\text{py,steam}}$ is the steam consumption in the pyrolysis process, in t·h^{-1}; $f^{\text{py,steam}}$ denotes the steam consumption factor in the pyrolysis process, in t(steam)·t(feed oil)$^{-1}$. The superscripts py, bohdt, FCC, dhdt and ghdt are the pyrolysis, bio-oil HDT, FCC, diesel HDT and gasoline HDT processes, respectively.

The electricity consumption of the fast pyrolysis and its following HDT process and the catalytic pyrolysis can be calculated by feed stream flowrate and the electricity consumption factor [15, 16], which are shown in eq(88) and eq(89), respectively. The electricity consumed in FCC, FCC diesel HDT and FCC gasoline HDT are obtained from their operating instructions and technical monthly reports, respectively.

$$W_i^{\text{py,elec}} = m_i^{\text{pqnc,bo,out}} f_i^{\text{py,elec}} \tag{88}$$

$$W_i^{\text{bohdt,elec}} = m_i^{\text{bohdt,in}} f^{\text{bohdt,elec}} \tag{89}$$

$$W_i^{\text{FCC,elec}} = m_i^{\text{FCC,in}} f_i^{\text{FCC,elec}} \tag{90}$$

$$W_i^{\text{dhdt,elec}} = m_i^{\text{dfp,oil,in}} f^{\text{dhdt,elec}} \tag{91}$$

$$W_i^{\text{ghdt,elec}} = m_i^{\text{gfp,oil,in}} f^{\text{ghdt,elec}} \tag{92}$$

where $W_i^{\text{py,elec}}$ is electricity consumption in pyrolysis process, in kW; $f_i^{\text{py,elec}}$ denote the factor of electricity consumption, in kW·t^{-1}.

1.2.2 Steam and electricity generations

In the co-processing system, the steam consumed in the pyrolysis processes and bio-oil HDT process is come from the boiler, while the electricity is from power grid. The existing utility plant of the refinery is used to satisfy all demands of steam and electricity in the FCC, FCC diesel HDT and FCC gasoline HDT. Thus, the steam generation for the pyrolysis processes and bio-oil HDT process is only considered.

$$m_i^{\text{sd,steam}} = m_i^{\text{py,steam}} + m_i^{\text{bohdt,steam}} \tag{93}$$

where $m_i^{\text{sd,steam}}$ is total steam generation in the steam drum, in t.

1.3 Utility consumptions

1.3.1 Water

The water consumption of each process can be calculated by the flowrate of the feed stream multiplying by the water consumption factor, which are shown in eqs(94) and (95). The water consumptions of the FCC, the FCC diesel HDT and the FCC gasoline HDT are derived from their operating instructions and technical monthly reports, respectively.

$$m_i^{\text{py,water}} = m_i^{\text{pgrd,bms,in}} f_i^{\text{py,water}} \tag{94}$$

$$m_i^{\text{bohdt,water}} = m_i^{\text{bohdt,in}} f_i^{\text{bohdt,water}} \tag{95}$$

where $m_i^{\text{py,water}}$ is the water consumption in the pyrolysis process, in t·h^{-1}; $f^{\text{py,water}}$ denotes the water consumption factor in the pyrolysis process, in t(water)·t(feed oil)$^{-1}$.

1.3.2 Hydrogen

The hydrogen consumption of fast pyrolysis oil HDT is mainly consist of the HDO and other hydrogen consumption, like the dissolution and loss of hydrogen. The HDO consumption can be calculated by eq(97).

$$m_i^{\text{bohdt,H}_2} = m_i^{\text{bohdt,HDO}} + m_i^{\text{bohdt,OH}} \tag{96}$$

$$m_i^{\mathrm{bohdt,HDO}}=0.00445 v_i^{\mathrm{bohdt,in}}\left(O_i^{\mathrm{bohdt,in}}-O_i^{\mathrm{bohdt,out}}\right) \tag{97}$$

where $m_i^{\mathrm{bohdt,H_2}}$ is the total hydrogen consumption of the bio-oil HDT process, in $\mathrm{Nm^3 \cdot h^{-1}}$; $m_i^{\mathrm{bohdt,HDO}}$ denotes the hydrogen consumption of HDO reaction, in $\mathrm{Nm^3 \cdot h^{-1}}$; $m_i^{\mathrm{bohdt,OH}}$ represents other hydrogen consumption, in $\mathrm{Nm^3 \cdot h^{-1}}$; $v_i^{\mathrm{bohdt,in}}$ is volumetric flowrate of the feed oil in bio-oil HDT process, in $\mathrm{m^3 \cdot h^{-1}}$; $O_i^{\mathrm{bohdt,in}}$ and $O_i^{\mathrm{bohdt,out}}$ are the oxygen contents of the inlet and outlet streams in the HDT reactor, in %. The superscripts HDO and OH denote the hydrogen consumption of HDO reaction and other hydrogen consumption, respectively.

As for the FCC diesel HDT process, its hydrogen consumption mainly contains the hydrodesulfuration (HDS), hydrodenitrogenation (HDN), saturation of aromatics (HDA), the HDO and other hydrogen consumption. The hydrogen consumptions of HDS, HDN, HDA and HDO are expressed by eqs(98)~(102).

$$m_i^{\mathrm{dhdt,H_2}} = m_i^{\mathrm{dhdt,HDS}} + m_i^{\mathrm{dhdt,HDN}} + m_i^{\mathrm{dhdt,HDA}} + m_i^{\mathrm{dhdt,HDO}} + m_i^{\mathrm{dhdt,OH}} \tag{98}$$

$$m_i^{\mathrm{dhdt,HDS}}=0.0023 v_i^{\mathrm{dhdt,in}}\left(S_i^{\mathrm{dhdt,in}}-S_i^{\mathrm{dhdt,out}}\right) \tag{99}$$

$$m_i^{\mathrm{dhdt,HDN}}=0.0062 v_i^{\mathrm{dhdt,in}}\left(N_i^{\mathrm{dhdt,in}}-N_i^{\mathrm{dhdt,out}}\right) \tag{100}$$

$$m_i^{\mathrm{dhdt,HDA}}=480 v_i^{\mathrm{dhdt,in}}\left(A_i^{\mathrm{dhdt,in}}-A_i^{\mathrm{dhdt,out}}\right) \tag{101}$$

$$m_i^{\mathrm{dhdt,HDO}}=0.00445 v_i^{\mathrm{dhdt,in}}\left(O_i^{\mathrm{dhdt,in}}-O_i^{\mathrm{dhdt,out}}\right) \tag{102}$$

where the superscripts HDS, HDN, HDA and HDO are the hydrogen consumptions of the HDS, HDN, HDA and HDO reactions, respectively. S and N denote the sulfur and nitrogen contents, in ppm; A is the aromatics content, in %.

For the FCC gasoline HDT process, the hydrogen consumption is similar to the one in diesel HDT process, it can be calculated by eqs(103)~(107).

$$m_i^{\mathrm{ghdt,H_2}} = m_i^{\mathrm{ghdt,HDS}} + m_i^{\mathrm{ghdt,HDN}} + m_i^{\mathrm{ghdt,HDA}} + m_i^{\mathrm{ghdt,HDO}} + m_i^{\mathrm{ghdt,OH}} \tag{103}$$

$$m_i^{\mathrm{ghdt,HDS}}=0.0023 v_i^{\mathrm{ghdt,in}}\left(S_i^{\mathrm{ghdt,in}}-S_i^{\mathrm{ghdt,out}}\right) \tag{104}$$

$$m_i^{\text{ghdt,HDN}}=0.0062 v_i^{\text{ghdt,in}}\left(N_i^{\text{ghdt,in}}-N_i^{\text{ghdt,out}}\right) \tag{105}$$

$$m_i^{\text{ghdt,HDA}}=480 v_i^{\text{ghdt,in}}\left(A_i^{\text{ghdt,in}}-A_i^{\text{ghdt,out}}\right) \tag{106}$$

$$m_i^{\text{ghdt,HDO}}=0.00445 v_i^{\text{ghdt,in}}\left(O_i^{\text{ghdt,in}}-O_i^{\text{ghdt,out}}\right) \tag{107}$$

The total hydrogen consumption of the co-processing process is the sum of the above-mentioned HDT processes.

The product yields of FCC with different temperatures and densities are listed in Table S1. The data are retrieved from monthly technical reports.

Table S1 Product yields of FCC with different temperatures and densities

Process	Products	Yield / %			
		Feed oil density / kg·m^{-3}		Operating temperature / °C	
		875.47	880.21	495	510
FCC	Gas	18.9	18.2	18	22.2
	Gasoline	45.8	45.6	48.1	48.5
	Diesel	26.1	26.0	23	20.8
	Slurry oil	3.5	3.7	5.9	0.5

Nomenclature

Parameters

a, b calculation coefficients of impurity distributions

f utility consumption factor

p utility prices, \$·kWh^{-1}, \$·MJ^{-1} and \$·t^{-1}

y product yield of reactor or separator, %

Variables

A aromatics content, %

m mass flowrate or utility consumption, t·h^{-1}, kW and MJ·h^{-1}

N nitrogen content, ppm

O	oxygen content, % or ppm
S	sulfur content, ppm

Superscripts

A	aromatics
ac	air compressor
air	air blowing to an air compressor
bc	bio-char
bfp	feed pump in bio-oil HDT process
bfur	furnace in bio-oil HDT process
bg	bio-gas
bmhc	make-up hydrogen compressor in bio-oil HDT process
bms	biomass
bo	bio-oil
bohdt	bio-oil HDT process
bot	bottom stream
brct	reactor in bio-oil HDT
brhc	recycling hydrogen compressor in bio-oil HDT process
bsep	separator in bio-oil HDT process
cat	catalyst
comp	compressor
d	discharge stream of a compressor

dfp	feed pump in diesel HDT process
dfur	furnace in diesel HDT process
dhdt	diesel HDT process
ds	diesel
dmhc	make-up hydrogen compressor in diesel HDT process
drct	reactor in diesel HDT process
drhc	recycling hydrogen compressor in diesel HDT process
dtur	turbine in diesel HDT process
exh	exhaust
elec	electricity
FCC	fluid catalytic cracker
feed	feed
FG	fuel gas
gas	gas
gfp	feed pump in gasoline HDT process
gfur	furnace in gasoline HDT process
ghdt	gasoline HDT process
gmhc	make-up hydrogen compressor in gasoline HDT process
grct	reactor in gasoline HDT process
grhc	recycling hydrogen compressor in gasoline HDT process
gs	gasoline

gtur	turbine in gasoline HDT process
H_2	hydrogen
hbo	hydrotreated bio-oil
HDA	hydrogen consumption of HDA reaction
HDN	hydrogen consumption of HDN reaction
HDO	hydrogen consumption of HDO reaction
HDS	hydrogen consumption of HDS reaction
heater	heater
in	inlet stream
N	nitrogen
O	oxygen
OH	other hydrogen consumption
other	other
out	outlet stream
P	products
pcvt	convertor in pyrolysis process
pcyl	cyclone in pyrolysis process
pdry	drier in pyrolysis process
pfur	furnace in pyrolysis process
pgrad	grinder in pyrolysis process
ppyr	pyrolysis reactor in pyrolysis process

pqnc quench in pyrolysis process

psplt splitter in pyrolysis process

py pyrolysis process

pump pump

s suction stream of a compressor

S sulfur

sand sand

so slurry oil

steam steam

top top stream

U utilities

up upper bound

VGO vacuum gas oil

water water

Subscripts

i set of bio-oil production processes, i.e. fast pyrolysis or catalytic pyrolysis

Reference

1. L. Wu, Y. Wang, L. Zheng, M. Shi and J. Li, *Energy Conversion and Management*, 2019, **195**, 620-629.
2. Q. Zhang, J. Gong, M. Skwarczek, D. Yue and F. You, *AIChE Journal*, 2014, **60**, 980-994.
3. Z. Yuan and M. R. Eden, *AIChE Journal*, 2016, **62**, 3155-3176.
4. , !!! INVALID CITATION !!! 2-4.
5. T. Kan, V. Strezov and T. J. Evans, *Renewable and Sustainable Energy Reviews*, 2016, **57**, 1126-1140.

6. J. K. Satyarthi, T. Chiranjeevi, D. T. Gokak and P. S. Viswanathan, *Fuel Processing Technology*, 2014, **118**, 180-186.
7. A. Aho, N. Kumar, K. Eränen, T. Salmi, M. Hupa and D. Y. Murzin, *Fuel*, 2008, **87**, 2493-2501.
8. S. van Dyk, J. Su, J. D. McMillan and J. Saddler, *Biofuels, Bioproducts and Biorefining*, 2019, **13**, 760-775.
9. C. Liu, J. Liu, G. Zhou, W. Tian and L. Rong, *Journal of the Taiwan Institute of Chemical Engineers*, 2013, **44**, 221-227.
10. M. Al Jamri, R. Smith and J. Li, in *Computer Aided Chemical Engineering*, Elsevier, 2019, vol. 46, pp. 991-996.
11. L. Wu, Y. Liu and Q. Zhang, *Energy & Fuels*, 2017, **31**, 9850-9862.
12. A. d. R. Pinho, M. B. B. de Almeida, F. L. Mendes, L. C. Casavechia, M. S. Talmadge, C. M. Kinchin and H. L. Chum, *Fuel*, 2017, **188**, 462-473.
13. L. Gueudré, F. Chapon, C. Mirodatos, Y. Schuurman, R. Venderbosch, E. Jordan, S. Wellach and R. M. Gutierrez, *Fuel*, 2017, **192**, 60-70.
14. L. Wu, Y. Wang, L. Zheng, X. Han and F. Hong, *Industrial & Engineering Chemistry Research*, 2018, **57**, 15785-15793.
15. M. M. Wright, D. E. Daugaard, J. A. Satrio and R. C. Brown, *Fuel*, 2010, **89**, S2-S10.
16. Q. Li, Y. Zhang and G. Hu, *Bioresource technology*, 2015, **191**, 88-96.