Supporting Information

Sustainable DMC production from CO_2 and renewable ammonia and methanol

Antonio Sánchez[a], **Luis M. Gil**[a], **Mariano Martín**[a1]

[a]Department of Chemical Engineering. University of Salamanca. Plz. Caídos 1-5. 37008.
Salamanca (Spain)

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[1] Corresponding author. Tel.: +34 923294479
Email address: mariano.m3@usal.es

1. Modelling issues

Some modelling details are included in this section to deepen the information given in the main text.

1.1 Vapour-Liquid Equilibrium (VLE) in urea synthesis

Vapour-Liquid Equilibrium (VLE) is used in the urea synthesis section to describe the performance of the system in spite of the conditions are supercritical [1-3]. The equation to implement this VLE are as eq.(S1). The main equation that describes the VLE is [2]:

$$P y_i \phi_i = f_i^0 x_i \gamma_i \tag{S1}$$

Where P is the total pressure, y_i is the molar fraction per component i, ϕ_i is the fugacity coefficient, f_i^0 is the fugacity, x_i is the liquid molar fraction and γ_i is the activity coefficient.

For the most ideal case, the following assumptions hold:

$$\phi_i = 1 \ ; \ \gamma_i = 1 \ ; \ f_i^0 = P_i^0 \tag{S2}$$

Where P_i^0 is the vapour pressure for each component. The vapour pressures for the species involved in the system were computed using Antoine equations from the literature [4] or fitting experimental data or from rigorous simulation to an equation in the same form that the Antoine equation.

Therefore, the VLE equation takes the following form:

$$K = \frac{y_i}{x_i} = \frac{P_i^0}{P} \tag{S3}$$

Where K is the VL equilibrium constant. This relationship is joined to the mass balances to compute the vapour and liquid fraction depends on the operating conditions (pressure, temperature and composition).

$$F = L + V \tag{S4}$$

$$F z_i = L x_i + V y_i \tag{S5}$$

$$\sum_i y_i = 1 \tag{S6}$$

$$\sum_i x_i = 1 \tag{S7}$$

1.2 Urea Reactor

The urea reactor is modelled based on the correlation for the conversion presented in eq.(3). The mass and energy balances that with the conversion modelled this unit are as follow (based on reactions eq.(1)-(2)):

$$fc_{Carbamate}^{out} = fc_{CO_2}^{in} + fc_{Carbamate}^{in} - \left(fc_{Urea}^{out} - fc_{Urea}^{in} \right) \tag{S8}$$

$$fc_{Urea}^{out} = X \cdot \left(fc_{Urea}^{in} + fc_{CO_2}^{in} + fc_{Carbamate}^{in} \right) \tag{S9}$$

$$fc_{H_2O}^{out} = fc_{H_2O}^{in} + \left(fc_{Urea}^{out} - fc_{Urea}^{in} \right) \tag{S10}$$

$$fc_{NH_3}^{out} = fc_{NH_3}^{in} - 2\, fc_{CO_2}^{in} \tag{S11}$$

$$\sum_i fc_i^{in} h_i^{in} + \Delta H_{reac1} fc_{CO_2}^{in} = \sum_i fc_i^{out} h_i^{out} + \Delta H_{reac2} \left(fc_{Urea}^{out} - fc_{Urea}^{in} \right) \tag{S12}$$

fc_i is the molar flow per component i, X is the conversion of the second urea reaction, h_i is the enthalpy for each component, ΔH_{reac1} is the heat of reaction for the first urea reaction (-159 kJ/kmol of carbamate) and ΔH_{reac2} is the heat of reaction for the second urea reaction (31.4 kJ/kmol of urea).

1.3 Urea stripper

The urea stripper is modelled based on a surrogate model that compute the liquid yield for each specie involved (see section 3.1.2 in the main text). The yields are calculated with the following equations:

$$
\begin{aligned}
\mathrm{R}_{Urea} = {} & -518.215028200482-0.284950725834463\cdot \mathrm{P}+2.95476072757198\cdot \mathrm{T}+1.80131942015766\cdot\left(\frac{Q}{U}\right)\\
& -217.645482840702\cdot\left(\frac{U}{NH_3}\right)+144.322612155776\cdot\left(\frac{U}{H_2O}\right)-23.4997562338943\cdot\left(\frac{U}{CO_2}\right)\\
& -18.6482710341462\cdot\left(\frac{U}{CO_{2IN}}\right)-0.000625187050143106\cdot \mathrm{P}\cdot \mathrm{P}-0.00358947384425963\cdot T\cdot T\\
& -0.00159480074579542\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{Q}{U}\right)-43.6916212334017\cdot\left(\frac{U}{NH_3}\right)\cdot\left(\frac{U}{NH_3}\right)\\
& +0.000883129727668199\cdot \mathrm{P}\cdot \mathrm{T}+0.123968437321115\cdot \mathrm{P}\cdot\left(\frac{U}{NH_3}\right)-0.00357027639984928\cdot \mathrm{T}\cdot\left(\frac{Q}{U}\right)\\
& +0.508817144975195\cdot T\cdot\left(\frac{U}{NH_3}\right)-0.33575712211819\cdot T\cdot\left(\frac{U}{H_2O}\right)\\
& +0.0559892272569286\cdot T\cdot\left(\frac{U}{CO_2}\right)+0.0441381847036554\cdot T\cdot\left(\frac{U}{CO_{2IN}}\right)\\
& -0.280993398880857\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{H_2O}\right)+23.8479014645434\cdot\left(\frac{U}{NH_3}\right)\cdot\left(\frac{U}{H_2O}\right)
\end{aligned}
\tag{S13}
$$

$$
\begin{aligned}
\mathrm{R}_{NH_3} = {} & 363.421008053347+1.02283207923837\cdot \mathrm{P}-1.6865849816883\cdot \mathrm{T}\\
& -1.42886596581643\cdot\left(\frac{Q}{U}\right)+1.89678432914491\cdot\left(\frac{U}{NH_3}\right)\\
& -173.541185790149\cdot\left(\frac{U}{H_2O}\right)+2.13291242076277\cdot\left(\frac{U}{CO_2}\right)\\
& +80.6413084986838\cdot\left(\frac{U}{CO_{2IN}}\right)+0.00191115498901465\cdot T\cdot T\\
& +61.2980445456304\cdot\left(\frac{U}{H_2O}\right)\cdot\left(\frac{U}{H_2O}\right)-0.00195433955988442\cdot \mathrm{P}\cdot \mathrm{T}\\
& -0.00213339921678927\cdot \mathrm{P}\cdot\left(\frac{Q}{U}\right)-0.192442657544106\cdot \mathrm{P}\cdot\left(\frac{U}{H_2O}\right)\\
& +0.122348143496973\cdot P\cdot\left(\frac{U}{CO_{2IN}}\right)+0.00369827528484878\cdot \mathrm{T}\cdot\left(\frac{Q}{U}\right)\\
& +0.280508392193704\cdot T\cdot\left(\frac{U}{H_2O}\right)-0.17092502627161\,5\cdot T\cdot\left(\frac{U}{CO_{2IN}}\right)\\
& +0.247064145229264\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{H_2O}\right)-0.183712997636469\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{CO_{2IN}}\right)\\
& -14.8974151859256\cdot\left(\frac{U}{H_2O}\right)\cdot\left(\frac{U}{CO_{2IN}}\right)
\end{aligned}
\tag{S14}
$$

$$\begin{aligned}
\mathrm{R}_{CO_2} ={}&-24.6820636152254+0.222380812733441\cdot \mathrm{P}+0.177196824184314\cdot \mathrm{T}\\
&-0.0141855991019543\cdot\left(\frac{Q}{U}\right)-59.1242003629388\cdot\left(\frac{U}{NH_3}\right)-15.4525458485839\cdot\left(\frac{U}{H_2O}\right)\\
&-9.03647006314354\cdot\left(\frac{U}{CO_2}\right)-0.854264129513543\cdot\left(\frac{U}{CO_{2IN}}\right)-0.000219146793932474\cdot T\cdot T\\
&+19.3825862013371\cdot\left(\frac{U}{H_2O}\right)\cdot\left(\frac{U}{H_2O}\right)-3.05683312723582\cdot\left(\frac{U}{CO_{2IN}}\right)\cdot\left(\frac{U}{CO_{2IN}}\right)\\
&-0.000461882393429577\cdot \mathrm{P}\cdot \mathrm{T}-0.0880742901622562\cdot \mathrm{P}\cdot\left(\frac{U}{H_2O}\right)\\
&+0.0539665938430128\cdot \mathrm{P}\cdot\left(\frac{U}{CO_2}\right)+0.0559983482606198\cdot P\cdot\left(\frac{U}{CO_{2IN}}\right)\\
&+0.124371549409968\cdot \mathrm{T}\cdot\left(\frac{U}{NH_3}\right)+0.0896301599303116\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{NH_3}\right)\\
&-0.0612997203229086\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{CO_{2IN}}\right)+5.12639174859366\cdot\left(\frac{U}{CO_2}\right)\cdot\left(\frac{U}{CO_{2IN}}\right)
\end{aligned}\tag{S15}$$

$$\begin{aligned}
\mathrm{R}_{H_2O} ={}&415.656146379107-1.40951201488907\cdot \mathrm{P}-0.806726309737707\cdot \mathrm{T}\\
&+3.5522739160318\cdot\left(\frac{Q}{U}\right)-268.1249557368\cdot\left(\frac{U}{NH_3}\right)\\
&+237.93460634717\cdot\left(\frac{U}{H_2O}\right)+7.65189731042131\cdot\left(\frac{U}{CO_2}\right)\\
&+8.66265209434843\cdot\left(\frac{U}{CO_{2IN}}\right)+0.00317313232439402\cdot \mathrm{P}\cdot \mathrm{T}\\
&-0.00764567556523745\cdot T\cdot\left(\frac{Q}{U}\right)+0.669844549831203\cdot T\cdot\left(\frac{U}{NH_3}\right)\\
&-0.548994997976013\cdot T\cdot\left(\frac{U}{H_2O}\right)-0.680329653858759\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{H_2O}\right)
\end{aligned}\tag{S16}$$

$$\begin{aligned} \mathrm{T}_{liquid}^{out} = {} & 180.074822916299-1.29647750539426\cdot \mathrm{P}+0.537306963368549\cdot \mathrm{T} \\ & +3.30253577898588\cdot\left(\frac{Q}{U}\right)+635.378632760966\cdot\left(\frac{U}{NH_3}\right) \\ & -1.4887132676095\cdot\left(\frac{U}{H_2O}\right)-9.08774528270758\cdot\left(\frac{U}{CO_2}\right) \\ & -211.483091694472\cdot\left(\frac{U}{CO_{2IN}}\right)+0.00243789836116356\cdot \mathrm{P}\cdot \mathrm{T} \\ & +0.440497648476484\cdot \mathrm{P}\cdot\left(\frac{U}{NH_3}\right)-0.00460841793394988\cdot \mathrm{T}\cdot\left(\frac{Q}{U}\right) \\ & -1.42689653407166\cdot \mathrm{T}\cdot\left(\frac{U}{NH_3}\right)+0.502790812183236\cdot \mathrm{T}\cdot\left(\frac{U}{CO_{2IN}}\right) \\ & +1.45095567309948\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{H_2O}\right)-0.0256532339924944\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{CO_2}\right) \end{aligned} \tag{S17}$$

$$\begin{aligned} \mathrm{T}_{gas}^{out} = {} & 56.6201838288691+0.0000150301463124054\cdot \mathrm{P} \\ & +0.864243130532875\cdot \mathrm{T}-1.71036819173564\cdot\left(\frac{Q}{U}\right) \\ & +93.7078150219783\cdot\left(\frac{U}{NH_3}\right)-111.514440146262\cdot\left(\frac{U}{H_2O}\right) \\ & -2.25327122002595\cdot\left(\frac{U}{CO_2}\right)+6.51724015832229\cdot\left(\frac{U}{CO_{2IN}}\right) \\ & +0.00398684220198224\cdot \mathrm{T}\cdot\left(\frac{Q}{U}\right)-0.207737654112389\cdot \mathrm{T}\cdot\left(\frac{U}{NH_3}\right) \\ & +0.219116462750508\cdot \mathrm{T}\cdot\left(\frac{U}{H_2O}\right)+0.76534937413338\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{NH_3}\right) \\ & +0.509782670009266\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{H_2O}\right)-0.165851633915337\cdot\left(\frac{Q}{U}\right)\cdot\left(\frac{U}{CO_{2IN}}\right) \end{aligned} \tag{S18}$$

The surrogate models have been developed for the following operating ranges:

$$140 \le P(bar) \le 200 \tag{S19}$$

$$443 \le T(K) \le 493 \tag{S20}$$

$$20 \le \left(\frac{Q}{U}\right)\left(\frac{MJ}{kmol}\right) \le 50 \tag{S21}$$

$$0.2 \le \left(\frac{U}{NH_3} \right) \left(\frac{kmol}{kmol} \right) \le 0.5 \tag{S22}$$

$$0.4 \le \left(\frac{U}{H_2O} \right) \left(\frac{kmol}{kmol} \right) \le 0.7 \tag{S23}$$

$$0.9 \le \left(\frac{U}{CO_2} \right) \left(\frac{kmol}{kmol} \right) \le 1.4 \tag{S24}$$

$$0.9 \le \left(\frac{U}{CO_{2in}} \right) \left(\frac{kmol}{kmol} \right) \le 1.4 \tag{S25}$$

The total mass balances in the stripper unit are as follow:

$$fc_{Urea}^{liq} = \left(\frac{R_{Urea}}{100} \right) fc_{Urea}^{in} \tag{S26}$$

$$fc_{Urea}^{in} = fc_{Urea}^{liq} + fc_{Urea}^{gas} \tag{S27}$$

$$fc_{NH_3}^{liq} = \left(\frac{R_{NH_3}}{100} \right) \left(fc_{NH3}^{in} + 2\, fc_{Carbamate}^{in} \right) \tag{S28}$$

$$fc_{NH_3}^{in} + 2\, fc_{Carbamate}^{in} = fc_{NH_3}^{liq} + fc_{NH_3}^{gas} \tag{S29}$$

$$fc_{CO_2}^{liq} = \left(\frac{R_{CO_2}}{100} \right) \left(fc_{CO_2}^{in} + fc_{Carbamate}^{in} \right) \tag{S30}$$

$$fc_{CO_2}^{in} + fc_{Carbamate}^{in} = fc_{CO_2}^{liq} + fc_{CO_2}^{gas} \tag{S31}$$

$$fc_{H_2O}^{liq} = \left(\frac{R_{H_2O}}{100} \right) fc_{H_2O}^{in} \tag{S32}$$

$$fc_{H_2O}^{in} = fc_{H_2O}^{liq} + fc_{H_2O}^{gas} \tag{S33}$$

1.4 Urea condenser

In the urea condenser, the reaction that forms ammonium carbamate takes place. The reaction is controlled by the heat removed in this unit. The conversion is limited by the heat balances in the urea reactor. The following mass and energy balances described the urea condenser performance:

$$fc_{Urea}^{in/mix2} = fc_{Urea}^{out} \tag{S34}$$

$$fc_{H_2O}^{in/mix1} + fc_{H_2O}^{in/mix2} = fc_{H_2O}^{out} \tag{S35}$$

$$fc_{CO_2}^{in/mix1} + fc_{CO_2}^{in/mix2} = fc_{Carbamate}^{out} + fc_{CO_2}^{out} \tag{S36}$$

$$fc_{NH_3}^{in/mix1} + fc_{NH_3}^{in/mix2} = fc_{NH_3}^{out} + 2\, fc_{Carbamate}^{out} \tag{S37}$$

$$\sum_i fc_i^{in/mix1} h_i^{in/mix1} + \sum_i fc_i^{in/mix2} h_i^{in/mix2} = \sum_i fc_i^{out} h_i^{out} + \Delta H_{reac1}\, fc_{Carbamate}^{out} \tag{S38}$$

1.5 First DMC reactor

The first DMC reactor (Reac2) is modelled considering a conversion equal to 100% and an isotherm and isobaric system. The pressure is fixed to 20 bar and the temperature to 423K [5]. The mass and energy balances are as follows:

$$fc_{NH_3}^{in} + fc_{Urea}^{in} = fc_{NH_3}^{out} \tag{S39}$$

$$fc_{Urea}^{in} = fc_{MC}^{out} \tag{S40}$$

$$fc_{MeOH}^{in} - fc_{Urea}^{in} = fc_{MeOH}^{out} \tag{S41}$$

$$fc_{H_2O}^{in} = fc_{H_2O}^{out} \tag{S42}$$

$$fc_{DMC}^{in} = fc_{DMC}^{out} \tag{S43}$$

$$Q_{reac2} = \sum_i fc_i^{out} h_i^{out} + \Delta H_{reac3}\, fc_{MC}^{out} - \sum_i fc_i^{in} h_i^{in} \tag{S44}$$

Where ΔH_{reac3} is the heat of reaction for the methyl carbamate (MC) formation (-10310 kJ/kmol MC).

1.6 Second DMC Reactor

The second DMC reactor is modelled based on the experimental yield from the equation eq.(9). In this reactor, two reactions are involved: the DMC formation and the NMMC formation. The NNMC reaction is undesirable. The yields with the mass and energy balances determined the reactor performance:

$$fc_{DMC}^{out} = fc_{DMC}^{in} + Y_{DMC}\, fc_{MC}^{in} \tag{S45}$$

$$fc_{NMMC}^{out} = fc_{NMMC}^{in} + Y_{NMMC}\, fc_{MC}^{in} \tag{S46}$$

$$fc_{NH_3}^{out} = fc_{NH_3}^{in} + Y_{DMC}\, fc_{MC}^{in} + Y_{NMMC}\, fc_{MC}^{in} \tag{S47}$$

$$fc_{CO_2}^{in} = Y_{NMMC}\, fc_{MC}^{in} \tag{S48}$$

$$fc_{MeOH}^{out} = fc_{MeOH}^{in} - Y_{DMC}\, fc_{MC}^{in} \tag{S49}$$

$$fc_{MC}^{out} = fc_{MC}^{in} - Y_{DMC}\, fc_{MC}^{in} - 2Y_{NMMC}\, fc_{MC}^{in} \tag{S50}$$

$$fc_{H_2O}^{out} = fc_{H_2O}^{in} \tag{S51}$$

1.7 Distillation column: Fenske-Underwood-Gilliland (FUG) method

To describe the operation of distillation columns, the shortcut method of Fenske-Underwood-Gilliland (FUG) is used [6]. The fed stream enters in the column as saturated liquid and, therefore, at its bubble temperature. The distillate and the bottom stream are also saturated liquid. The following equations hold in a saturated liquid:

$$\sum_i K_i x_i = 1 \tag{S52}$$

$$K_i = \frac{P_{vap}^{i}}{P} \tag{S53}$$

In the saturated vapour streams hold the following relation:

$$\sum_i \frac{y_i}{K_i} = 1 \tag{S54}$$

The minimum number of stages is calculated using the Fenske equation:

$$N_m = \frac{\log\left[\left(\frac{x_{LD}D}{x_{HD}D}\right)\left(\frac{x_{HW}W}{x_{LW}W}\right)\right]}{\log\left(\alpha_{L,\mathrm{av}}\right)} \tag{S55}$$

Where LD is the key light component in the distillate, HD is the key heavy component in the distillate, HW is the key heavy component in the bottom and LW is the light key component in the bottom. $\alpha_{L,prom}$ is the average value of the relative volatility calculated as follow:

$$\alpha_{L,\mathrm{av}} = \sqrt{\alpha_{LD}\alpha_{LW}} \tag{S56}$$

The minimum reflux ratio is calculated with the two Underwood equations:

$$1 - q = \sum_i \frac{\alpha_i x_{iF}}{\alpha_i - \theta} \tag{S57}$$

$$R_m + 1 = \sum_i \frac{\alpha_i x_{iD}}{\alpha_i - \theta} \tag{S58}$$

Where q is the feed condition, θ is the underwood parameter and the volatility is calculated based on the average temperature in the column. To calculate the real reflux ratio, the following rule of thumb is used [7]:

$$R = 1.2R_{\mathrm{m}} \tag{S59}$$

The number of stages is calculated, for instance, with the empirical correlation or Erbar and Maddox [6].

2. Nomenclature

fc Molar flow

f_i^0 Fugacity

F Feed molar flow

h Enthalpy

K Equilibrium constant

L Liquid molar flow

N_m Minimum number of stages

P Pressure

P_i^0 Vapor pressure

q Feed condition

R_i Stripper yield

R_m Minimum reflux ratio

R Reflux ratio

V Molar vapor flow

x_i Molar fraction

X Conversion

y_i Molar faction

Y_i Reaction yield in Reac3

z_i Feed molar flow

ϕ_i Fugacity coefficient

γ_i Activity coefficient

ΔH Heat of reaction

α Volatility

3. References

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