

Supplemental Information for

**Polyolefin plastic waste hydroconversion to fuels, lubricants and
waxes: A comparative study**

Pavel A. Kots ^{1,†}, Brandon C. Vance ^{1,2,†}, Dionisios G. Vlachos ^{*,1,2}

Affiliations:

¹Center for Plastics Innovation, University of Delaware, 221 Academy St., Newark, DE 19716, USA

²Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy St., Newark, DE 19716, USA

[†]These authors contributed equally

Energy Analysis Calculations

The energy demand for the hydroconversion of polyolefins utilizes Eq-1 in the main text, reproduced here:

$$\Delta E_{demand} = \Delta E_{reactants} + \Delta E_{rxn} + \Delta E_{losses} \quad (1)$$

$\Delta E_{reactants}$ represents the energy needed to bring the reactants from the standard state (25 °C, 1 bar) to reaction conditions and is expressed as:

$$\Delta E_{reactants} = \Delta E_{heating}^{poly} + \Delta E_{compress}^{H_2} + \Delta E_{heating}^{H_2} \quad (S1)$$

The three terms correspond to the heating of polymer to reaction conditions, the isothermal compression of H₂ gas at 25 °C to reaction pressure, and heating the H₂ gas to reaction temperature, respectively. Each of these terms can be further expanded as:

$$\Delta E_{heating}^{poly} = [T_{rxn} - T_o]C_{ppoly} + \Delta \hat{H}_{poly}^{fus} \quad (S2)$$

$$\varphi \frac{\gamma R T_o}{\gamma - 1} \left(\frac{P_{rxn}}{P_o} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \quad (S3)$$

$$\int_{T_o}^{T_{rxn}} C_{pH_2} dT \quad (S4)$$

where T_o and P_o are the standard state temperature and pressure; T_{rxn} and P_{rxn} are the temperature and pressure at reaction conditions for a given processes; C_{ppoly} is the constant pressure specific heat capacity for PE¹ or PP²; $\Delta \hat{H}_{poly}^{fus}$ is the specific heat of fusion for PE or PP³; C_{pH_2} is the specific heat capacity function for H₂ using parameters reported by NIST; γ is the ratio of constant volume and constant pressure heat capacities for an ideal gas ($\gamma = 1.41$); R is the universal gas constant; and φ is the mass ratio of H₂ and polymer for a given process. The above equations reveal common assumptions in the simple analysis, such as temperature independent specific heat capacities, due to the lack of detailed thermochemistry for these complex systems.

ΔE_{rxn} in Eq-1 represents the energy of reaction to produce a reported product distribution at reaction conditions and can be expressed as:

$$\Delta E_{rxn} = n_{prod}(\Delta E_{rxn}^o + \Delta H^{ex}) \quad (S5)$$

The two terms correspond to the reaction energy at the standard state and excess enthalpy due to nonideal interactions of the product mixture, and n_{prod} is the total moles of the product.

ΔE_{rxn}^o is estimated in an approximate manner using differences in the bond energies⁴ for the overall hydroconversion reaction:

$$\Delta E_{rxn}^o = \Delta E_{C-C} + \Delta E_{H-H} - 2 \cdot \Delta E_{C-H} = [346 + 436 - 2(413)] \frac{kJ}{mol} = -\frac{44kJ}{mol} \quad (S6)$$

ΔH^{ex} was predicted using Aspen Plus™ for each product distribution for a given process and calculated using the “PENG-ROB” model.

ΔE_{losses} in Eq-1 is an estimate of the energy lost to the surrounds assuming all reactions were ran in a cylindrical, non-insulated 50 mL batch reactor with a radius of 9 cm and a height of 10 cm. ΔE_{losses} can be expressed as:

$$\Delta E_{losses} = t_{rxn} q'' A \quad (S7)$$

where t_{rxn} is the time of the reaction for a given process; A is the surface area of the reactor; and q'' is the heat flux from the reactor walls. We assumed the heat flux from the top and bottom of the reactor was negligible compared to the radial heat flux. Furthermore, we assumed heat transfer was at steady state and ignored the transient ramping period. Subsequently, a convective boundary condition at the reactor wall was applied to calculate q'' :

$$q'' = h(T_s - T_\infty) \quad (S8)$$

where h is the heat transfer coefficient; T_s is the temperature at the reactor wall; and T_∞ is the ambient air temperature (25 °C). To simplify the calculation, the temperature of the reactor wall was set equal to the reaction temperature:

$$T_s = T_{rxn} \quad (S9)$$

Eq-S10 correlates the heat transfer coefficient to the Nusselt number for cylindrical geometries (Nu_D):

$$Nu_D = \frac{hD}{k_f} \quad (S10)$$

where D is the diameter of the reactor and k_f is the thermal conductivity of air. We applied the Churchill-Bernstein equation⁵ to approximate Nu_D for the reactor:

$$Nu_D = 0.3 + \frac{0.62 Re_D^{1/2} Pr^{1/3}}{\left[1 + \left(\frac{0.4}{Pr}\right)^{2/3}\right]^{1/4}} \left[1 + \left(\frac{Re_D}{282,000}\right)^{5/8}\right]^{4/5} \quad (S11)$$

where Re_D is the Reynold's number for cylindrical geometries (Eq-S12) and Pr is the Prandtl number for air.

$$Re_D = \frac{UD}{\nu} \quad (S12)$$

where U is the bulk air velocity past the reactor and ν is the kinematic viscosity of the fluid. The bulk air velocity was set to the standard air face velocity of a laboratory hood (100 fpm, ~0.5 m/s). All physical properties of air (i.e., k_f , Pr , and ν) were evaluated at the film temperature (T_f) using interpolation of the air tables from Ref⁶:

$$T_f = \frac{T_o + T_\infty}{2} \quad (S13)$$

The Churchill-Bernstein equation is valid for all $Re_D Pr \gtrsim 0.2$ ⁵. The reaction temperatures (200 – 375 °C) result in $500 < Re_D Pr < 900$.

Sensitivity of the Energy Analysis

The sensitivity of the energy analysis results to deviations in reactor scale (D), assumed surface temperature (T_s), and reaction times (t) can be estimated by calculating the variation of ΔE_{demand} with respect to changes in each parameter:

$$\varepsilon_i \sim \frac{\partial}{\partial i}(\Delta E_{demand}) \quad (S14)$$

where ε is an estimate of the uncertainty in the given calculations with respect to variable $i = D, T_s, t$. We can substitute Eq-1 into Eq-S14 and distribute the partial derivative to each energy term to obtain:

$$\varepsilon_i \sim \frac{\partial}{\partial i}(\Delta E_{demand}) = \frac{\partial}{\partial i}(\Delta E_{reactants}) + \frac{\partial}{\partial i}(\Delta E_{rxn}) + \frac{\partial}{\partial i}(\Delta E_{losses}) \quad (S15)$$

$\Delta E_{reactants}$ are only sensitive to differences in T_{rxn} and P_{rxn} and are not functions of D , T_s , or t :

$$\frac{\partial}{\partial D}(\Delta E_{reactants}) = \frac{\partial}{\partial T_s}(\Delta E_{reactants}) = \frac{\partial}{\partial t}(\Delta E_{reactants}) = 0 \quad (S16)$$

ΔE_{rxn} is highly dependent on the catalytic system and its product distribution, which is a complex function of the reaction chemistry and reactor. Insufficient data is available to determine the deviations associated to ΔE_{rxn} . Subsequently, this deviation will serve as an intrinsic error that is unique to each catalytic system which we define as:

$$\epsilon_{rxn}^i \equiv \frac{\partial}{\partial i}(\Delta E_{rxn}) \quad (S17)$$

1. Sensitivity to Reaction Time

Starting with Eq-S15 and applying Eq-S16 – S18, we obtain:

$$\epsilon_t \sim \frac{\partial}{\partial t}(\Delta E_{losses}) + \epsilon_{rxn}^t \quad (S18)$$

The right hand side (RHS) of this expression can be evaluated further by substituting Eq-S7 in for ΔE_{losses} :

$$\epsilon_t \sim \frac{\partial}{\partial t}(t_{rxn} q'' A) + \epsilon_{rxn}^t \quad (S19)$$

q'' and A are independent of reaction time, thus Eq-S19 simplifies to:

$$\epsilon_t \sim \frac{\partial}{\partial t}(\Delta E_{demand}) = q'' A + \epsilon_{rxn}^t \quad (S20)$$

When deviations in reaction times are relatively small, it is reasonable to expect little change in a given product distribution, thus ϵ_{rxn}^t becomes negligible. Thus, the energy demand should scale directly with reaction time, given the product distribution does not change significantly.

2. Sensitivity to Surface Temperature

Again starting with Eq-S15, applying Eq-S16 – S18, and substituting Eq-S7 for ΔE_{losses} we obtain:

$$\varepsilon_{T_s} \sim \frac{\partial}{\partial T_s}(t_{rxn}q''A) + \epsilon_{rxn}^{T_s} \quad (S21)$$

Only q'' is dependent upon T_s via Eq-S8, thus:

$$\varepsilon_{T_s} \sim t_{rxn}A \frac{\partial}{\partial T_s}[h(T_s - T_\infty)] + \epsilon_{rxn}^{T_s} \quad (S22)$$

If we assume the physical properties of the film are constant, then h also becomes independent of T_s :

$$\varepsilon_{T_s} \sim \frac{\partial}{\partial T_s}(\Delta E_{demand}) = t_{rxn}Ah + \epsilon_{rxn}^{T_s} \quad (S23)$$

Ignoring $\epsilon_{rxn}^{T_s}$, Eq-S23 shows the energy demand will scale at a constant rate as the reactor surface temperature is varied. It is difficult to predict how $\epsilon_{rxn}^{T_s}$ will be affected when T_s is varied, especially if Eq-S9 holds as this will greatly alter the chemistry and product distribution. However, $\epsilon_{rxn}^{T_s}$ becomes zero if T_s and T_{rxn} are relatively independent, in the case the reactor is well-insulated or has a heating/cooling jacket.

3. Sensitivity to Reactor Diameter

Like the previous section, we start with Eq-S15, apply Eq-S16 – S18, and substitute Eq-S7 for ΔE_{losses} to obtain:

$$\varepsilon_D \sim \frac{\partial}{\partial D}(t_{rxn}q''A) + \epsilon_{rxn}^D \quad (S24)$$

A is directly dependent upon D , whereas q'' is indirectly dependent upon D through Eq-S8 and Eq-S10 – S12. If we substitute these equations in to Eq-S24 to get ε_D as a function of D , we obtain:

$$\varepsilon_D \sim t_{rxn}(T_s - T_\infty) \frac{\partial}{\partial D} \left[A \left(0.3 + \frac{0.62 \left(\frac{UD}{\nu} \right)^{1/2} Pr^{1/3}}{\left[1 + \left(\frac{0.4}{Pr} \right)^{2/3} \right]^{1/4}} \left[1 + \left(\frac{UD}{\nu 282,000} \right)^{5/8} \right]^{4/5} \right) \right] + \epsilon_{rxn}^D \quad (S25)$$

Continuing to assume the reactor has a cylindrical geometry of constant proportions between the reactor length and diameter (c), the area of reactor is:

$$A = \frac{\pi D^2}{2} + \pi D(cD) = \pi D^2 \left(c + \frac{1}{2} \right) \quad (S26)$$

Condensing terms containing constant parameters (t_{rxn} , T_s , T_∞ , U , ν , Pr , and c) into lumped variables:

$$\alpha \equiv t_{rxn} \pi (T_s - T_\infty) \left(c + \frac{1}{2} \right) \quad (S27)$$

$$\beta \equiv \frac{0.62 \left(\frac{U}{\nu} \right)^{1/2} Pr^{1/3}}{\left[1 + \left(\frac{0.4}{Pr} \right)^{2/3} \right]^{1/4}} \quad (S28)$$

$$\gamma \equiv \left(\frac{U}{\nu 282,000} \right)^{5/8} \quad (S29)$$

Eq-S25 simplifies to:

$$\varepsilon_D \sim \alpha \frac{\partial}{\partial D} \left[D^2 \left(0.3 + \beta D^{\frac{1}{2}} \left[1 + \gamma D^{5/8} \right]^{4/5} \right) \right] + \epsilon_{rxn}^D \quad (S30)$$

Evaluation of the derivative in Eq-S30 produces:

$$\varepsilon_D \sim \alpha \left[0.6D + \frac{\beta D^{\frac{3}{2}} \left(3\gamma D^{\frac{5}{8}} + \frac{5}{2} \right)}{\left(4 + \gamma D^{\frac{5}{8}} \right)^{\frac{5}{5}}} \right] + \epsilon_{rxn}^D \quad (S31)$$

An order of magnitude analysis on Eq-S31 can be used to simplify the dependence of ε_D :

$$\vartheta(\varepsilon_D) \approx D^2 + D^{\frac{11}{8}} + D \quad (S32)$$

From Eq-S32, it is clear the estimated energy demand and its sensitivity is strongly dependent on the reactor size. At small diameters, the energy demand is linearly dependent with respect to D , whereas at large diameters the energy demand is quadratically dependent upon D . Subsequently, variations in reactor scale can greatly impact the energy demand results. As for ϵ_{rxn}^D , it is reasonable to assume the diameter has a negligible impact on ϵ_{rxn}^D given the intrinsic kinetics of the catalytic systems. However, once the reactor scale becomes large enough that heat and mass transfer limitations begin to occur, ϵ_{rxn}^D will need to be considered.

References

- 1 Polyethylene - High density (HDPE) Material Information, <http://www.goodfellow.com/A/Polyethylene-High-density.html>, (accessed 28 September 2021).
- 2 Polypropylene (PP) Material Information, <http://www.goodfellow.com/E/Polypropylene.html>, (accessed 28 September 2021).
- 3 B. Wunderlich, *Thermal analysis*, Academic Press, 1990.
- 4 R. H. Petrucci, G. F. Herring, J. D. Madura and C. Bissonnette, *Petrucci, Harwood, Herring & Madura, General Chemistry: Principles and Modern Application & Basic Media Pack, 9th Edition / Pearson*, Pearson, Ninth., 2016.
- 5 S. W. Churchill and M. Bernstein, *J. Heat Transfer*, 1977, **99**, 300–306.
- 6 F. Incopera, D. Dewitt, T. Bergman and A. Lavine, *Fundamentals of Heat and Mass Transfer*, John Wiley & Sons, Inc., Sixth., 2015.