Hydrothermal liquefaction of by-products from the second-generation bioethanol industry

Carmina Reyes Plascencia[a,b], Matías Cagno[c], Pierre Cabot[c], Néstor Tancredi[a,b]

[a]Energías Renovables, IPTP, Facultad de Química, Universidad de la República, Pando, Uruguay.

[b]Fisicoquímica, Facultad de Química, Universidad de la República, Montevideo, Uruguay.

[c]Centro de Investigaciones en Biocombustibles 2G, Latitud – Fundación LATU, Montevideo, Uruguay.

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FACULTAD DE QUÍMICA

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RATIONALE

Aqueouse phase (C5, acids & furfural)

Steam Exploition → Slurry → Enzymatic Hydrolysis → Sugars & Acids → Fermentation → Bioethanol 2G

Pinus taeda sawdust

Wash water — Lignin-rich slurry

Hydrothermal liquefaction (HTL) by-products valorization
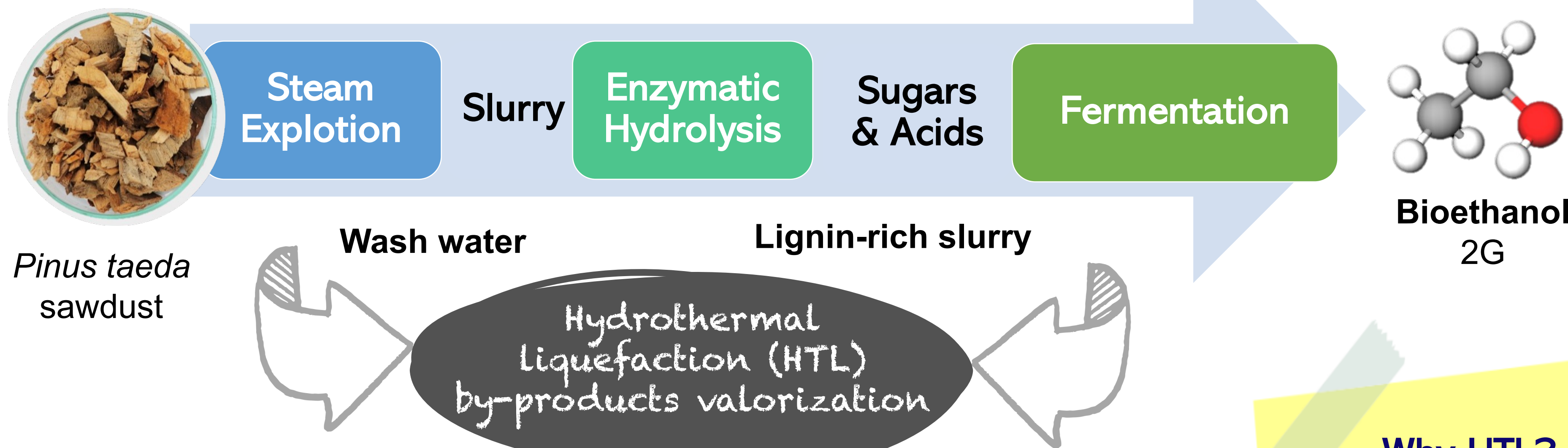
What is HTL?

Thermochemical transformations of biomass carried out in a solvent or water-rich environments at temperatures between **250 and 400 ºC and high pressures**, normally self-generated (5-25 MPa) for reaction times in the order of minutes.[1]

At these conditions, the intermediate molecules resulting from biomass hydrolysis undergo various chemical reactions such as condensation, cyclization, and polymerization leading to the formation of hydrophobic macromolecules, called **biocrude.**
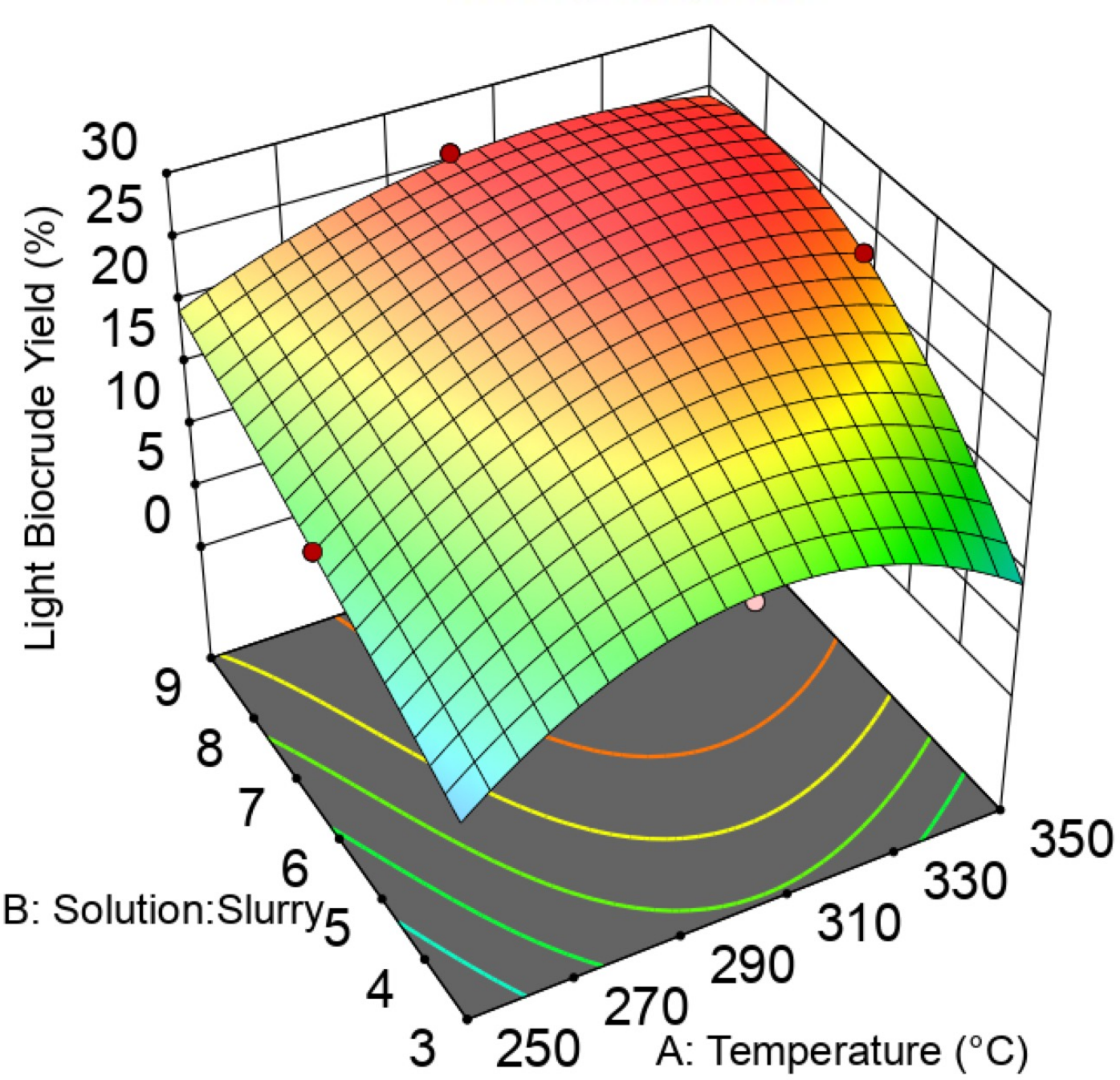
Why HTL?

Lignin-rich slurry has a high water content. Therefore LHT is desirable because the biomass does not need to be dried, so the energy loss linked to the drying process is avoided.
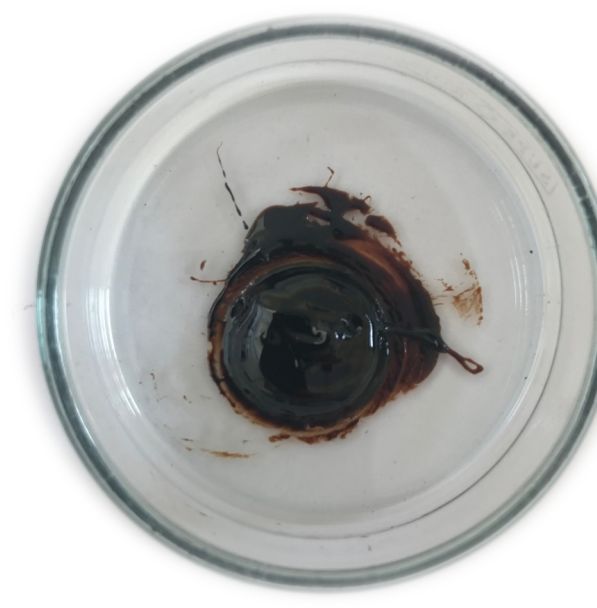
METHODOLOGY

Box–Behnken experimental design with three central points

Study varibles

Study varibles	
Temperture	250-350 ºC
Ethanol	0-100 %
Solution:Slurry*	1:1-9:1

* Dry slurry

Cube Std Error of Design

LHT conditions:

- Atmosphere: N_2
- Pressure: $P_{water} + P_{ethanol} + P_{productos}$
- Time: 90 min
- Slurry (d.b.): 22.5 g

Gas

Slurry
Acid-insoluble lignin: 58. 7 %
Moisture (w.b.): 75.47 %

+ Wash water / Ethanol

Volume 0.5 l

Filtration → Liquid / Solid ← Acetone

Liquid → Vacuum evaporation (80 ºC) → Water/Ethanol → **Light Biocrude**

Solid → Filtation → Hydrochar ; → Vacuum evaporation (35 ºC) → Acetone → **Heavy Biocrude**

Low Heating Value Calculation[2]

$$LHV\left(\frac{MJ}{kg}\right) = 38.2\frac{\%\,C}{100} + 84.9\left(\frac{\%\,H}{100} - \frac{\%\,O}{8*100}\right) - 0.5$$

RESULTS

Light Biocrude

2.9725 — 25.664

Light Biocrude Yield (%)

B: Solution:Slurry — A: Temperature (°C)

Coded Equation $R^2=0.9953$

+18.62	
+2.14	A
+4.59	B
+6.75	C
+0.58	AB
+2.69	AC
-1.94	A²
-3.10	B²
-1.64	C²
+2.44	A²B
-3.75	A²C
-2.90	AB²

Heavy Biocrude

2.4 — 41.1738

Heavy Biocrude Yield (%)

B: Solution:Slurry — A: Temperature (°C)
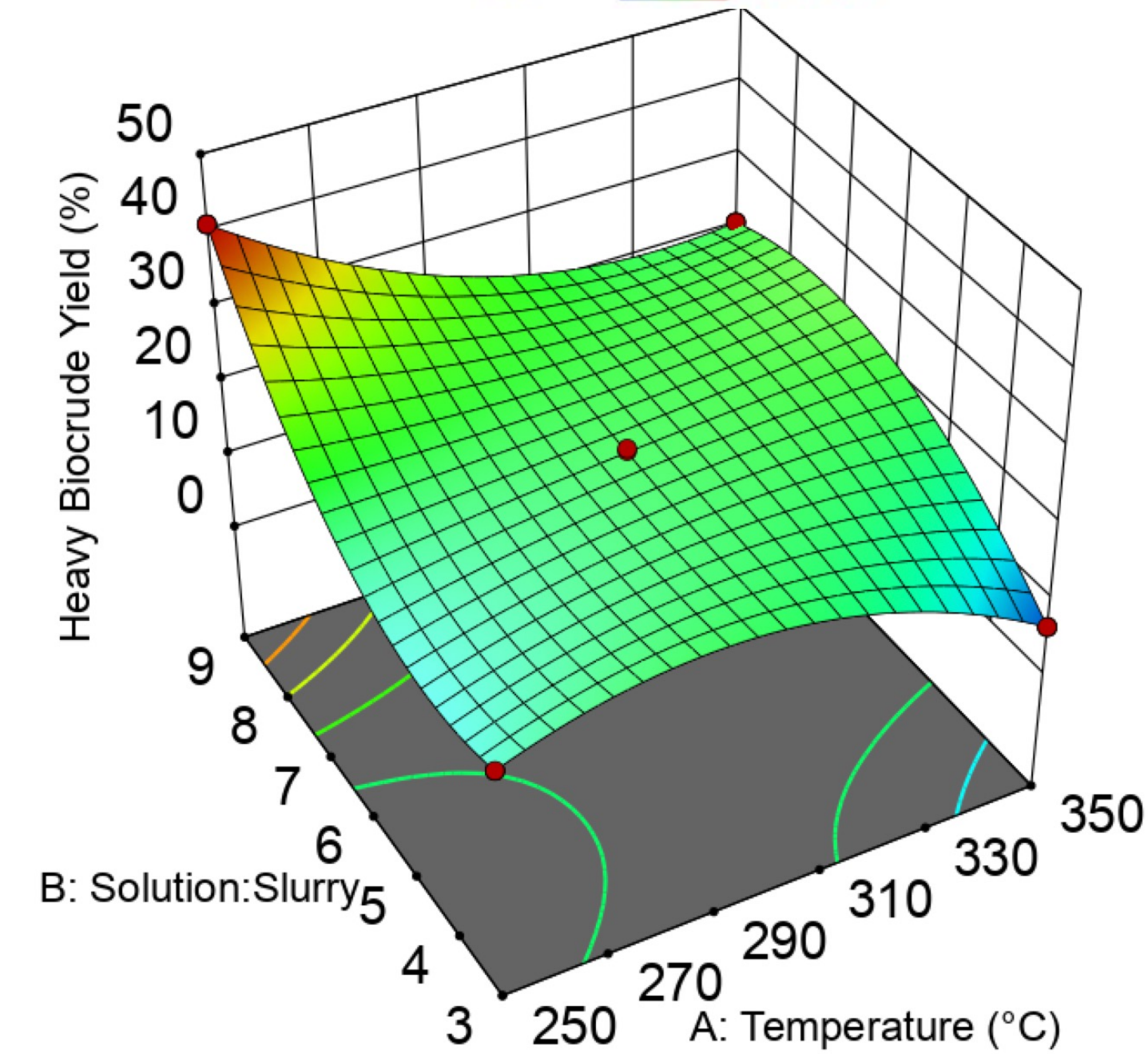
Coded Equation $R^2=0.9994$

+20.17	
+2.72	A
+2.13	B
-6.80	C
-2.98	AB
-2.61	AC
-2.02	BC
-0.78	A²
+1.41	B²
-12.05	C²
+8.07	A²B
+1.98	A²C
-9.91	AB²

Yield maximization

Light Biocrude
Temperature: 328.7 ºC
Ethanol: 96.6 %
Solution:Slurry: 7.6

Heavy Biocrude
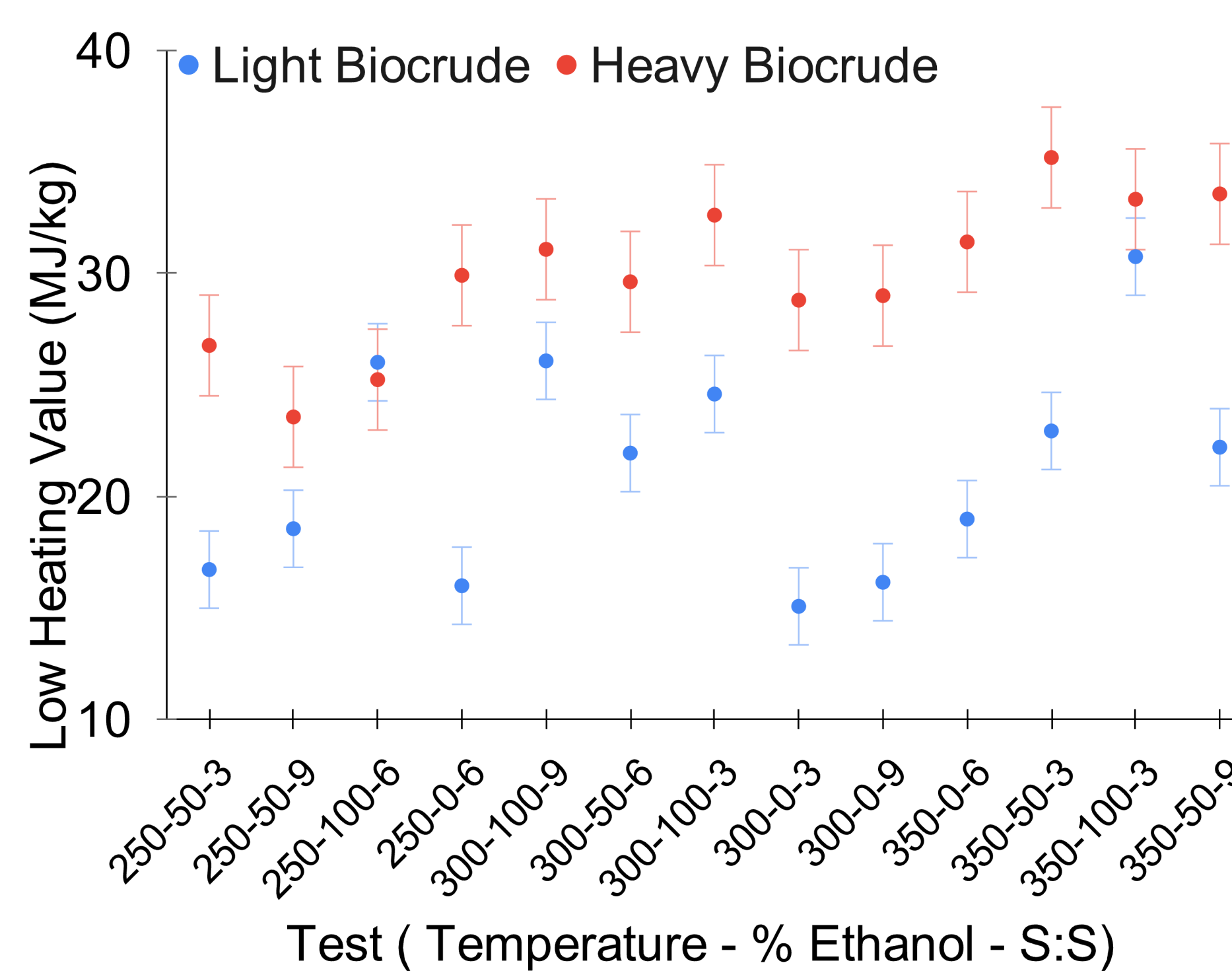Temperature: 250 ºC
Ethanol: 50 %
Solution:Slurry: 9

Low Heating Value (MJ/kg) — Light Biocrude — Heavy Biocrude

Test (Temperature - % Ethanol - S:S)

CONCLUSIONS

- It was possible to **optimize the yield** of light and heavy biocrude and **predict it** through the proposed experimental design.

- The **LHV** of **light biocrude** is in the range of **15.1-30.8 MJ kg⁻¹**, and the LHV of **heavy biocrude** is in the range of **23.6-33.6 MJ kg⁻¹.**

- Some **compounds of industrial interest** were identified, such as phenols and benzaldehydes.

- **LHT is a suitable process for producing liquid biofuels** from by-products of second-generation ethanol production.
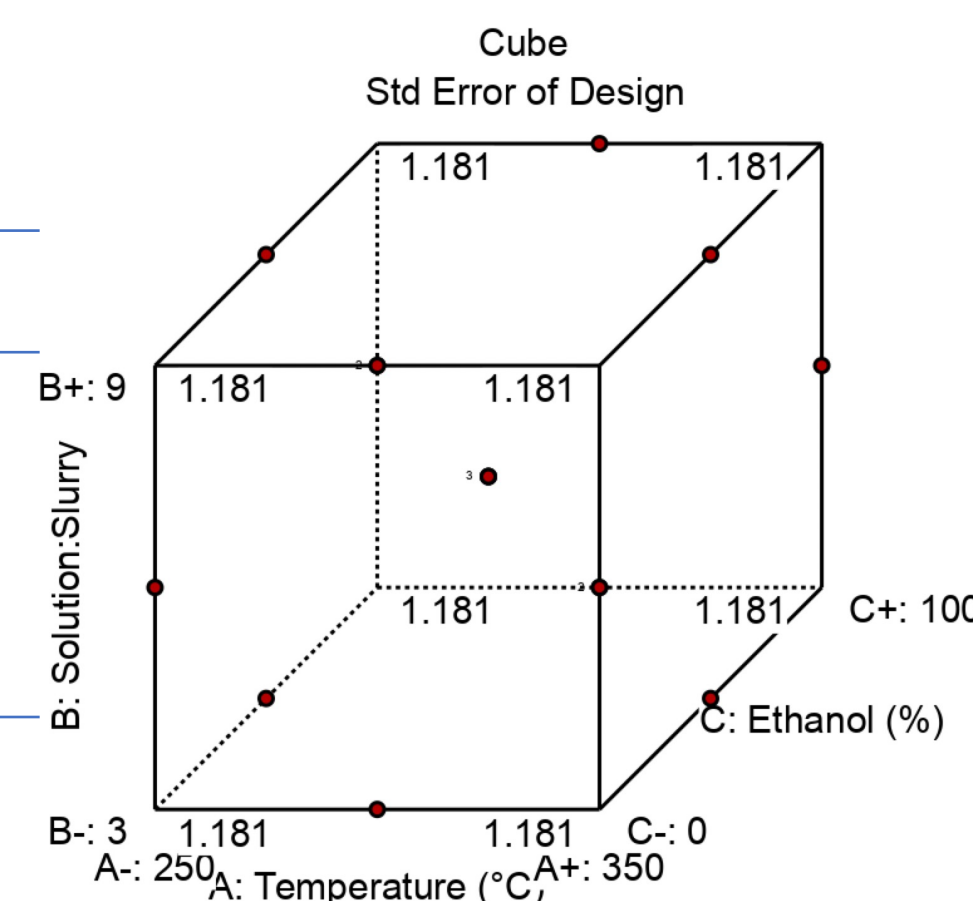
ACKNOWLEDGMENT

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[1]Delgado-Plaza, et al., 2022. Sustainability 15, 169.

[2]Sou Hosokai, et al., Fuel Processing Technology, 152, 399, 2016.