

## Supporting Information

### **Exploiting the Potential of Calcined Sodium Citrate as a novel and efficient heterogeneous catalyst for biodiesel synthesis**

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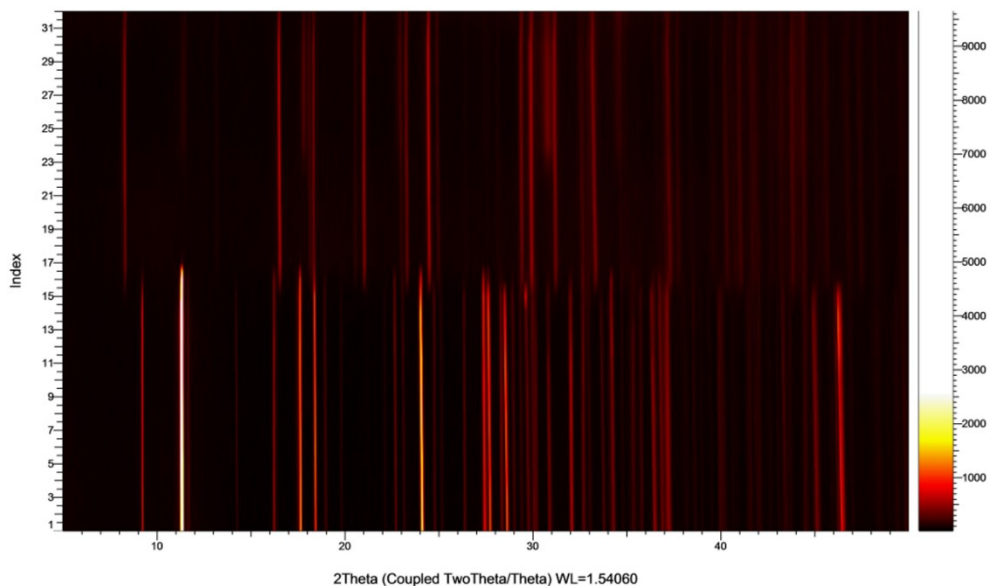
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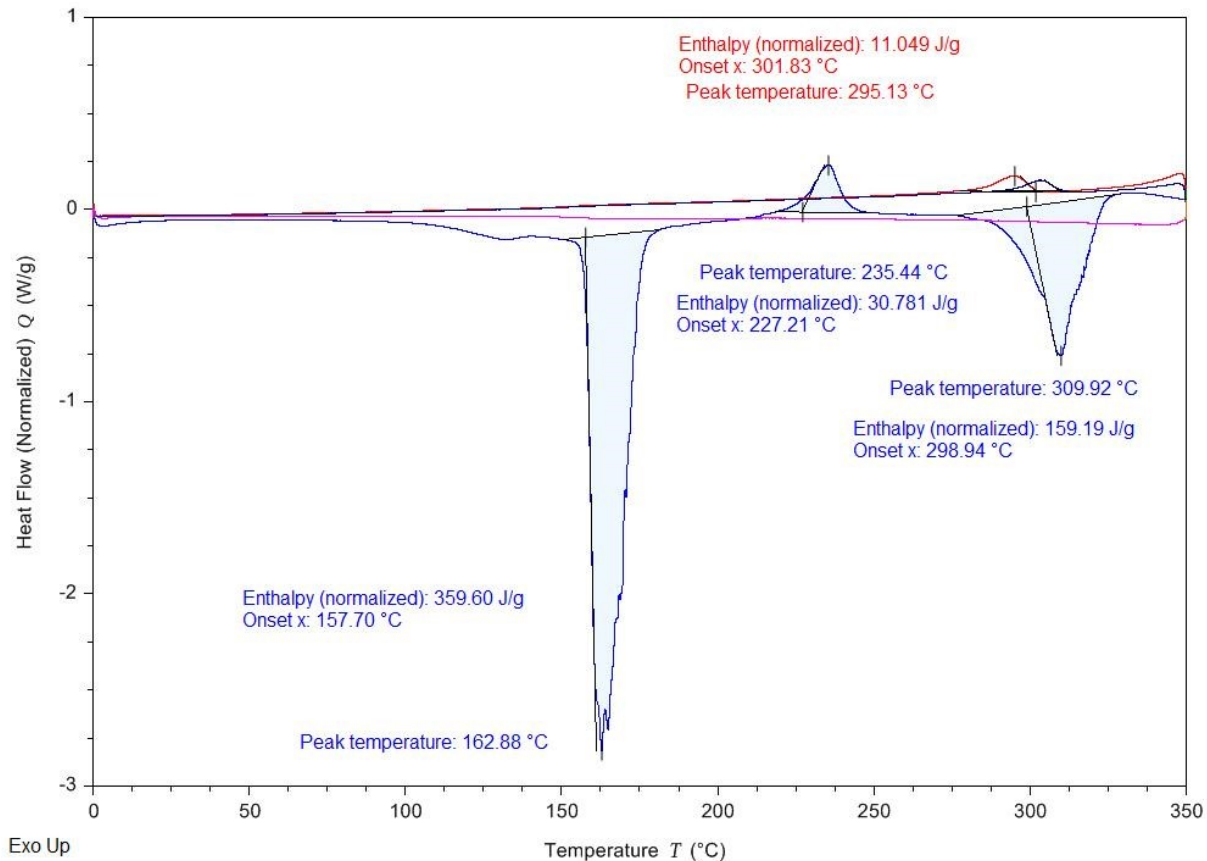
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## 1. Characterization of calcined sodium citrates

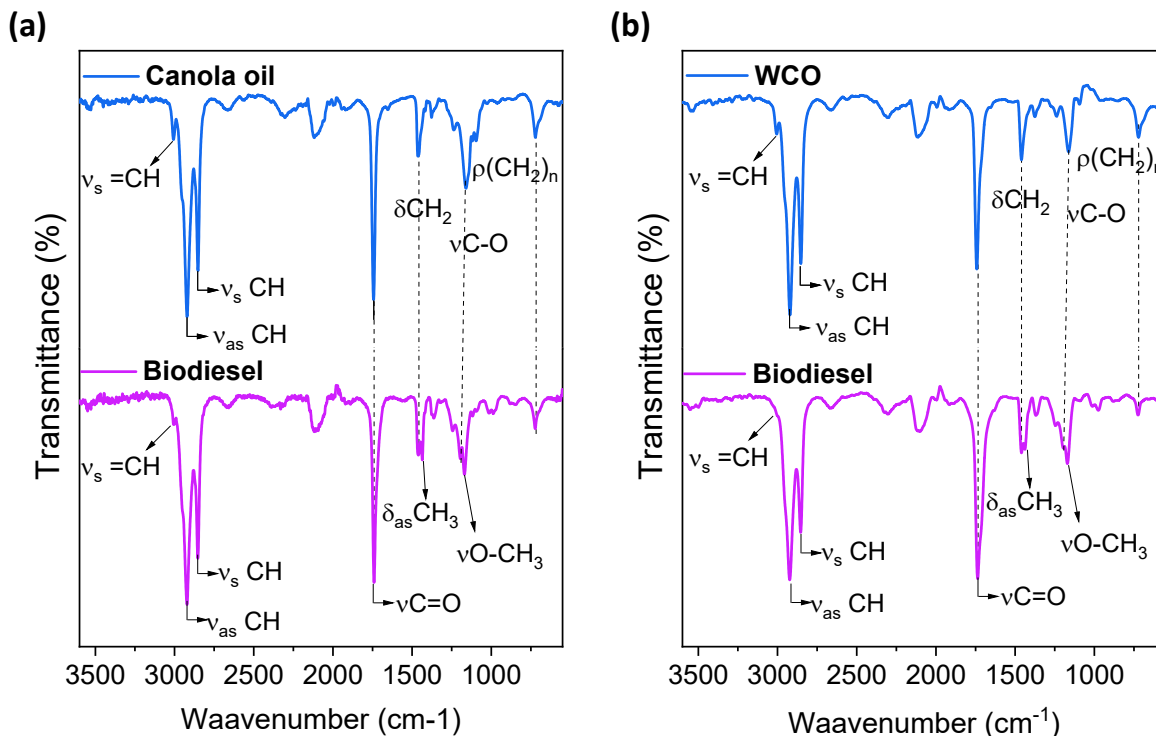


**Figure S. 1 (a)** Variable temperature powder X-ray diffraction (VT-PXRD) of sodium citrate in the range of 30 °C to 350 °C (10 °C/min). The formation of a new phase could be observed by the appearance of new reflections at 170 °C. These reflections are likely related to the change in the crystalline structure of sodium citrate due to the dehydration process. Furthermore, at 250 °C, additional reflections indicate further changes in the material's crystalline structure, resulting in the formation of new phase/phases.

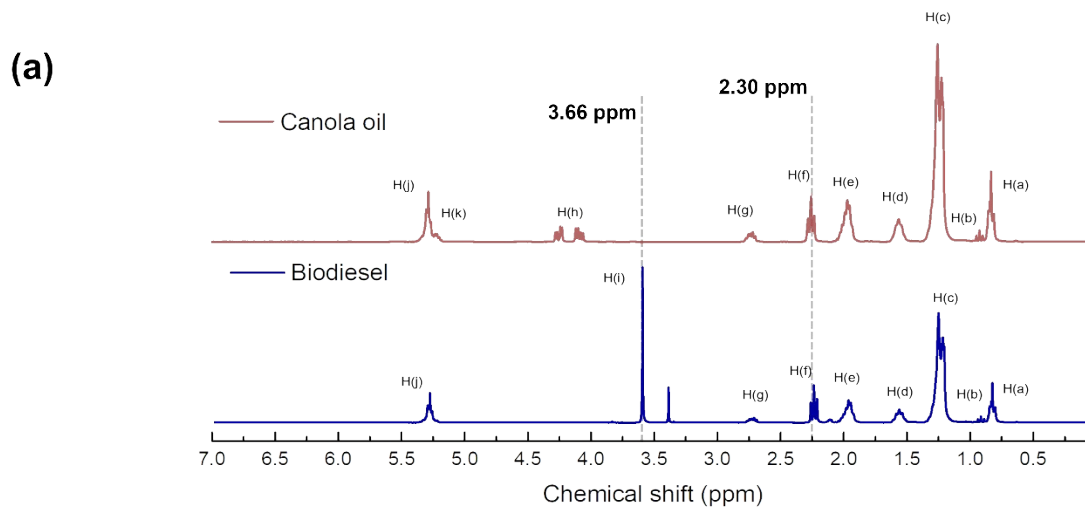


**Figure S. 2** DSC analysis of sodium citrate. From the thermogram, it is possible to observe an endothermic peak centered at 162.9 °C. This event corresponds to the loss of crystalline water from sodium citrate. An exothermic peak is observed at 245.4 °C, indicating a crystallization process. A second broad endothermic peak at 309.9 °C is noted and can be ascribed to the melting point of the different phases of sodium citrate formed during the heating process. During the cooling process, it is possible to note a small exothermic peak, related to the recrystallization of the material. These results corroborate the XRD pattern observed for sodium citrate calcined at different temperatures, as a first change in the crystalline structure is observed at 170 °C due to the loss of the crystalline water, followed by the changes at 250 °C, due to the formation of a new phase.

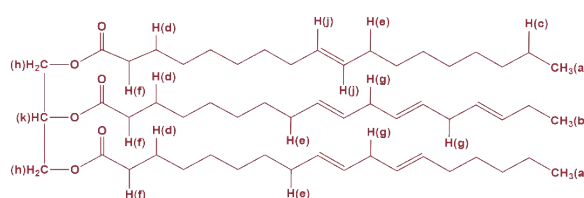
## 2. Characterization and quantification of biodiesel using FTIR and $^1\text{H}$ NMR



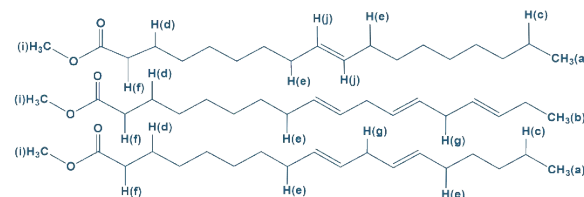
**Figure S. 3** FTIR spectra of (a) canola oil and biodiesel, (b) waste cooking oil and biodiesel, representing the characteristic vibrations associated with each material. Asymmetric and symmetric stretching vibrations associated with CH were observed at  $2929\text{ cm}^{-1}$ , and  $2855\text{ cm}^{-1}$ , respectively. A strong vibration stretch peak at  $1740\text{ cm}^{-1}$  attributed to C=O is also present in both. Besides that, the vibration at  $720\text{ cm}^{-1}$  indicates the methylene groups ( $-(\text{CH}_2)_n-$ ). Changes in spectra in the region of  $1400$  to  $1100\text{ cm}^{-1}$  confirm the conversion of canola and waste cooking oils into biodiesel. Vibrations at  $\sim 1460\text{ cm}^{-1}$  characteristic of  $\text{CH}_2$  bending were observed for both, while the bending associated with  $\text{CH}_3$  at  $\sim 1440\text{ cm}^{-1}$  is specific to biodiesel products. Furthermore, stretching attributed to O-CH<sub>3</sub> at  $1170\text{ cm}^{-1}$  is only observed for biodiesel products, whereas the stretch associated with -C-O-C at  $1160\text{ cm}^{-1}$  is evident for both.<sup>1</sup>



(b) Canola oil  $^1\text{H}$  NMR assignments



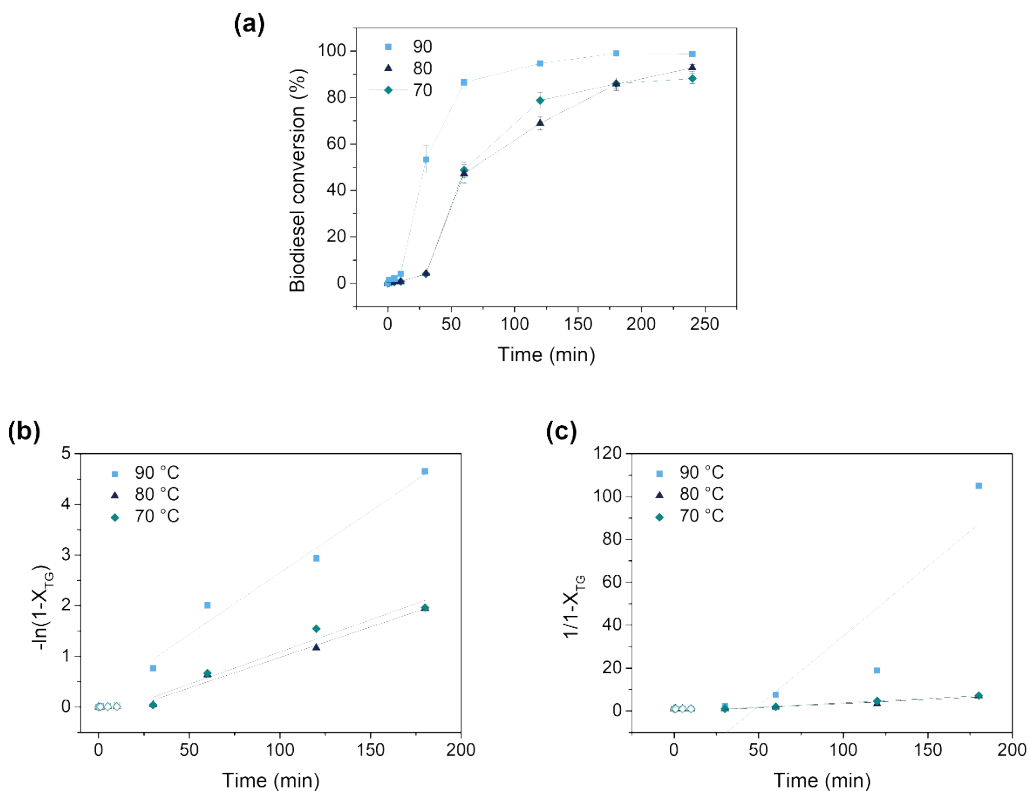
Biodiesel  $^1\text{H}$  NMR assignments



Assignments	Canola oil Chemical shift (ppm)	Biodiesel Chemical shift (ppm)
H(a)	0.88	0.88
H(b)	0.97	0.97
H(c)	1.25	1.26
H(d)	1.57	1.57
H(e)	1.96	1.96
H(f)	2.25	2.23
H(g)	2.75	2.74
H(h)	4.10; 4.24	-
H(i)	-	3.66
H(j)	5.30	5.30
H(k)	-	-

**Figure S.4 (a)**  $^1\text{H}$  NMR of canola oil and biodiesel obtained from the transesterification reactions. The quantification of the biodiesel yield is obtained by integrating the triplet associated with the  $\alpha$ -carbonyl protons (3.66 ppm) and the singlet associated with the methoxy protons (2.3 ppm). (b)  $^1\text{H}$  NMR assignments for canola oil and biodiesel.

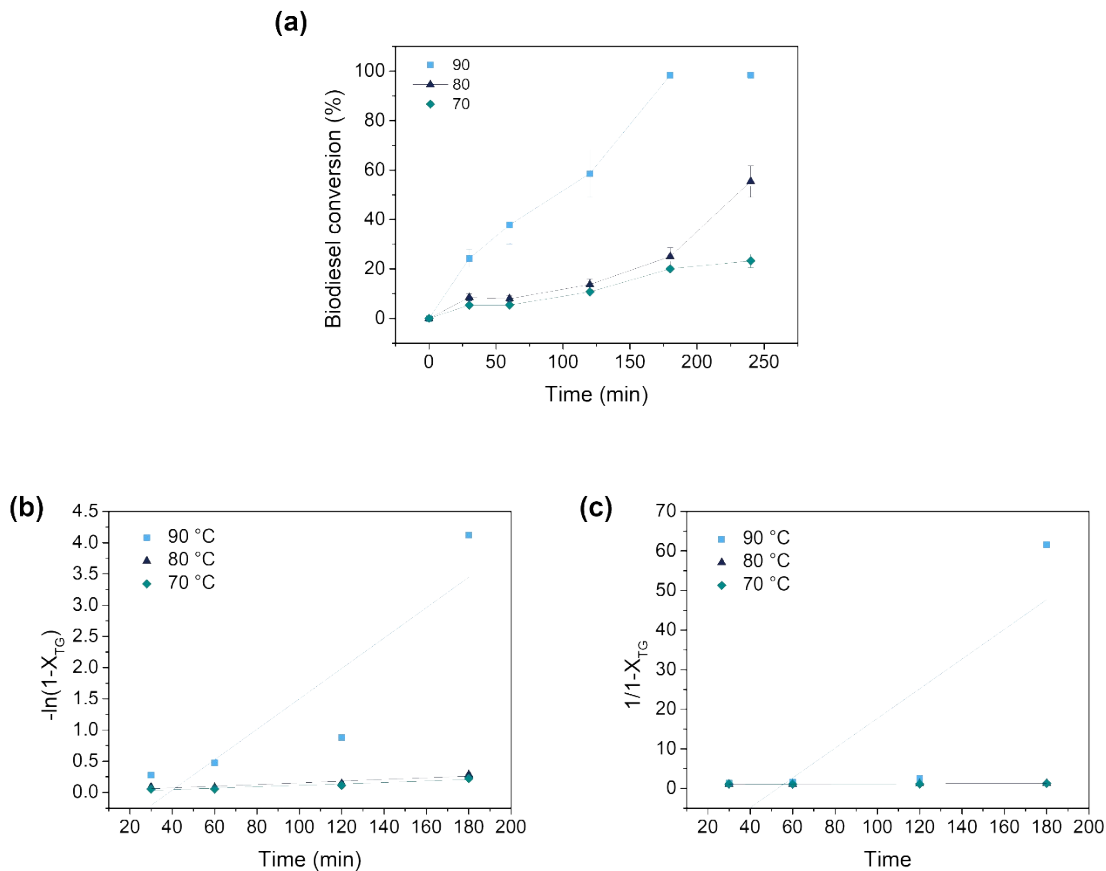
### 3. Kinetics studies of the transesterification of canola oil and waste cooking oil using calcined sodium citrate as a catalyst



**Figure S. 5** (a) Kinetic studies of the transesterification reaction of canola oil using calcined sodium citrate (250°C) as catalyst (b) Plot of  $-\ln(1-X_{TG})$  and (c)  $1/1-X_{TG}$  versus time at different temperatures. Reaction conditions: oil to methanol ratio of 1:9, catalyst loading of 3 wt.%.

**Table S. 1** Results of the adjustments of the kinetic models of pseudo-first order and pseudo-second order for the transesterification of canola oil using calcined sodium citrate (250°C) as the catalyst.

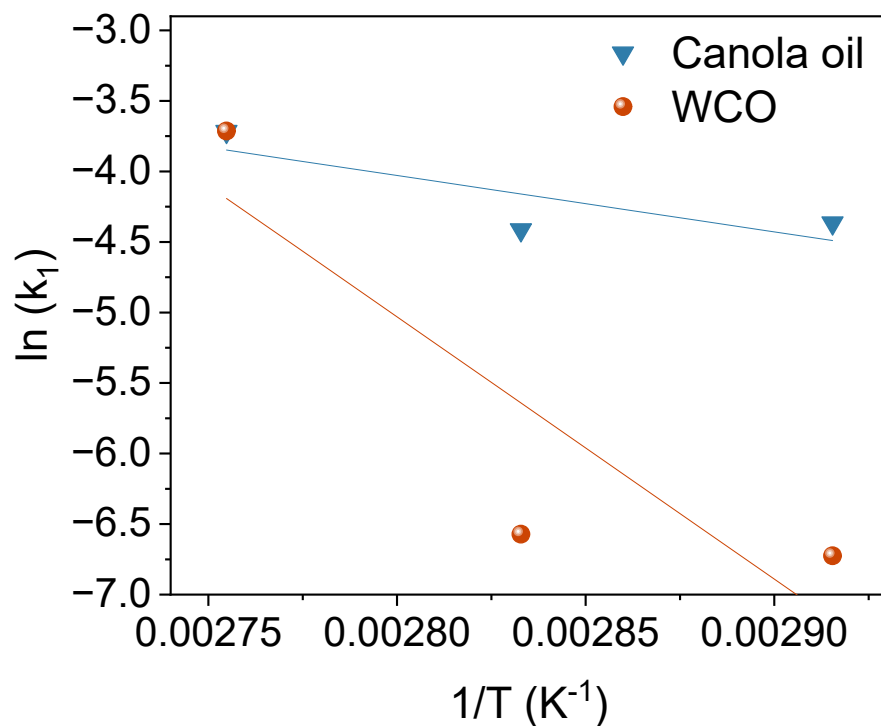
Temperature	Pseudo-first order		Pseudo-second order	
	$k_1, \text{min}^{-1}$	$R^2$	$k_2, \text{L/mol.min}$	$R^2$
70 °C	0.0127	0.9360	0.0546	0.9960
80 °C	0.0121	0.9762	0.0512	0.9062
90 °C	0.0243	0.9650	0.8606	0.7128



**Figure S. 6** (a) Kinetic studies of the (trans)esterification reaction of waste cooking oil using calcined sodium citrate (250°C) as catalyst (b) Plot of  $-\ln(1-X_{TG})$  and (c)  $1/(1-X_{TG})$  versus time at different temperatures. Reaction conditions: oil to methanol ratio of 1:36, catalyst loading of 10 wt.%.

**Table S. 2** Results of the adjustments of the kinetic models of pseudo-first order and pseudo-second order for the (trans)esterification of waste cooking oil using calcined sodium citrate (250°C) as the catalyst.

Temperature	Pseudo-first order		Pseudo-second order	
	$k_1, \text{min}^{-1}$	$R^2$	$k_2, \text{L/mol.min}$	$R^2$
70 °C	0.0012	0.8819	0.8947	0.8690
80 °C	0.0014	0.8398	0.0039	0.8245
90 °C	0.0244	0.7073	0.0031	0.5469



**Figure S. 7 (a)** Arrhenius plot for the transesterification of canola oil (▼) and WCO (●). It is possible to notice that an adequate adjustment of the experimental data to the Arrhenius linear model was not achieved for the (trans)esterification of waste cooking oil. The poor adjustment of this process was also noted in the kinetic models, which may be attributed to the significant impact of the temperature on the conversion of biodiesel.

#### References:

- 1 H. K. Imdadul, N. W. M. Zulkifli, H. H. Masjuki, M. A. Kalam, & M. Kamruzzaman, & M. M. Rashed, H. K. Rashedul and A. Alwi, *Env. Sci Pollut Res*, 2017, **24**, 2350–2363.