Biodiesel production *via* ethanolysis of jatropha oil using molybdenum impregnated calcium oxide as solid catalyst

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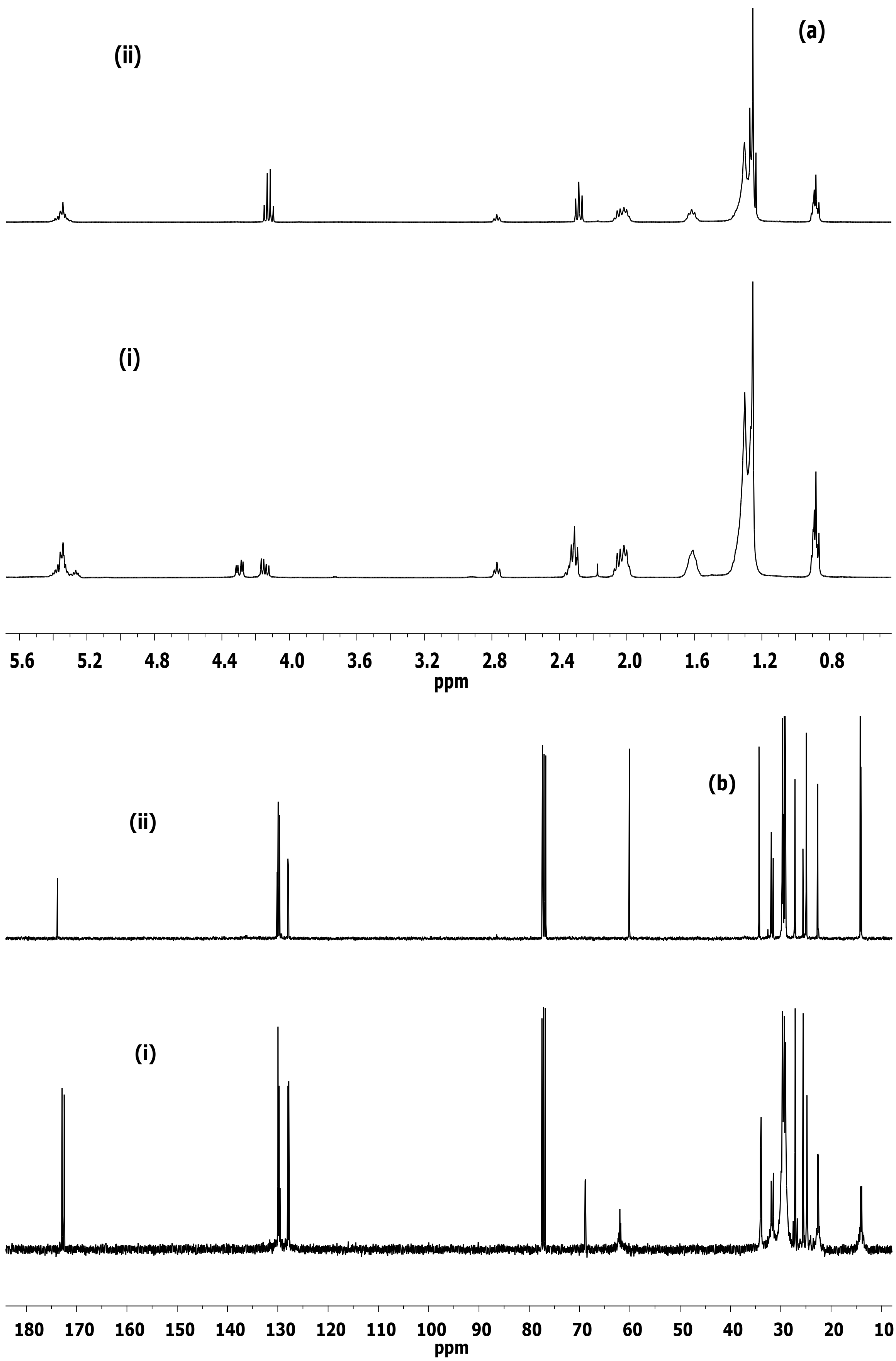

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g. S1. Comparison of (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of (i) jatropha oil with its (ii) ethyl esters.

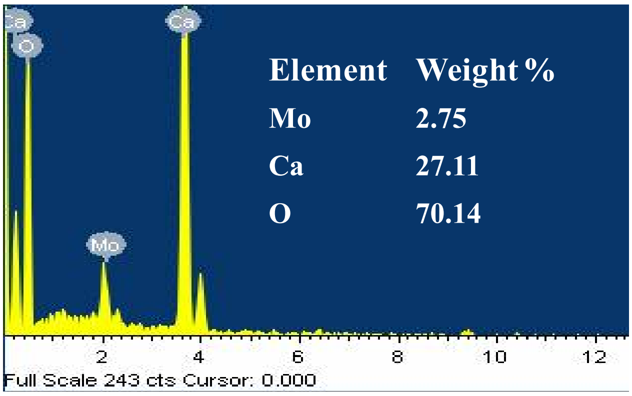

Fig. S2. EDX of 3Mo/CaO-700 catalyst.

Optimization of reaction parameters:

In order to examine the optimal catalyst concentration, a series of transesterification reactions of JO with ethanol were carried out in presence of 1–6 wt% (with respect to oil) of 3Mo/CaO-700 catalyst. As shown in Fig. S3(a), with the increase in catalyst concentration, the rate of reaction becomes faster because of the increase in the total number of available active sites for the transesterification reaction. A 5 wt% catalyst concentration required 4.5 h for the complete conversion of JO into FAEE (> 99% yield). The reaction rate was not enhanced to significant extent with further increase in catalyst concentration (≥ 5 wt%). This may be due to the higher mass transfer resistance at higher catalyst loading.[1]

According to the transesterification reaction, one mole of triglyceride requires three moles of ethanol for each mole of VO. Excess ethanol is applied to increase oil conversion by shifting the reaction equilibrium. The use of excess alcohol also removes product molecules from the catalyst surface and thus, regenerates the catalytic sites.[2] To determine the optimum ethanol/oil molar ratio for 3Mo/CaO-700, a series of transesterification reactions were performed by varying the ethanol/oil molar ratio from 3:1 to 15:1. The FAEE yield was found to increase on increasing the ethanol/oil molar ratios up to 12:1 and no significant gain in reaction rate was observed on increasing the molar ratio beyond 12, as shown in Fig. S3(b).

Reaction temperature can affect the reaction rate and the ester yield because the intrinsic rate constants are strong functions of temperature. Literature reported heterogeneous catalysts for the ethanolysis reaction works at high reaction temperature and pressure, due to the low reactivity of ethanol in comparison to methanol.[3,4] It demands the costlier and complicated reactor design which lead to increase the biodiesel production cost.[5] Fig. S3(c) shows the effect of the reaction temperature (35-75 ºC) on the FAEE yield. It indicates that the reaction rate was higher at high temperature and at ≥ 65 ºC, maximum reaction rate was observed.

Therefore, the optimum reaction temperature for the transesterification of JO to biodiesel is 65 °C.

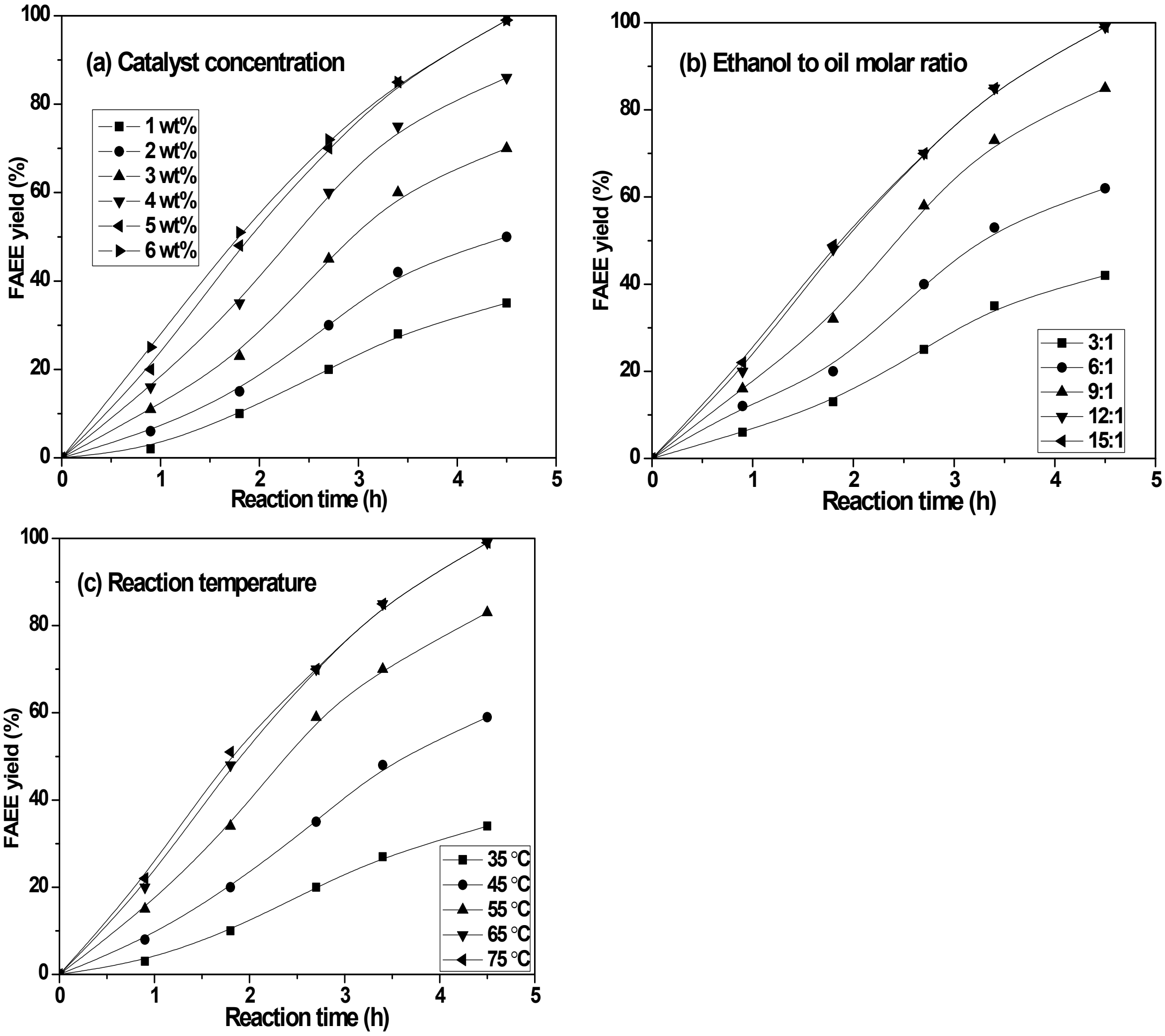

Fig S3. Effect of reaction parameters on 3Mo/CaO-700 catalyzed transesterification of JO. **Reaction conditions:-** (a) ethanol to oil molar ratio of 12:1 at 65 ºC reaction temperature (b) Reaction temperature at 65 ºC, in presence of 5 wt% of catalyst with respect to oil (c) ethanol to oil molar ratio of 12:1 in presence of 5 wt% of catalyst with respect to oil.

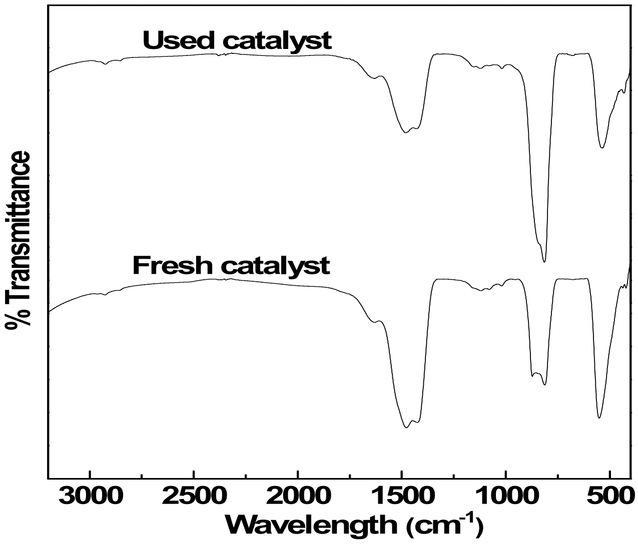

Fig. S4. Comparison of FT-IR of fresh and used catalyst.

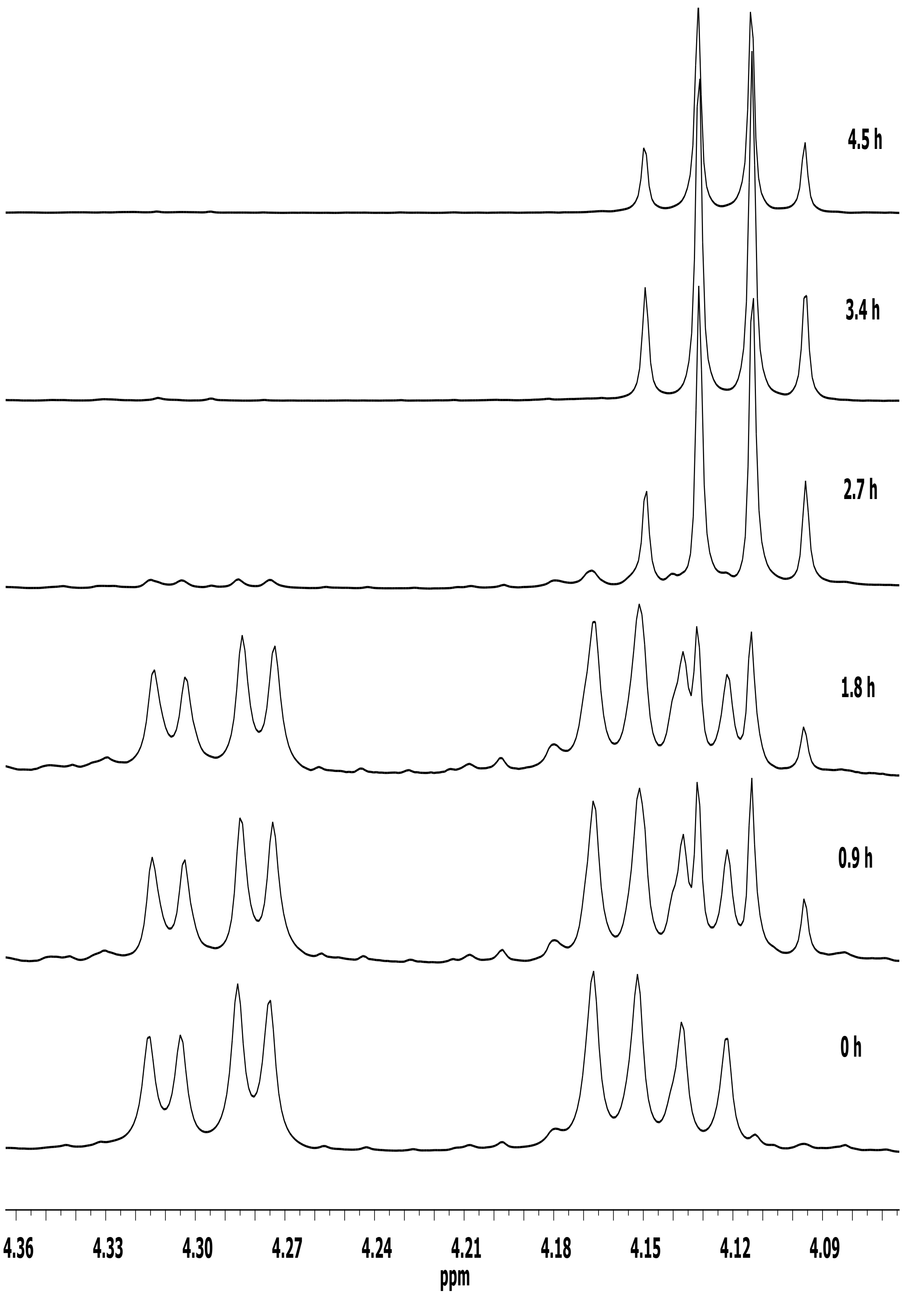

Fig. S5. Representative proton NMR spectra (4.0-4.36 ppm) of reaction mixture at various time intervals to study the kinetics of ethanolysis reaction.

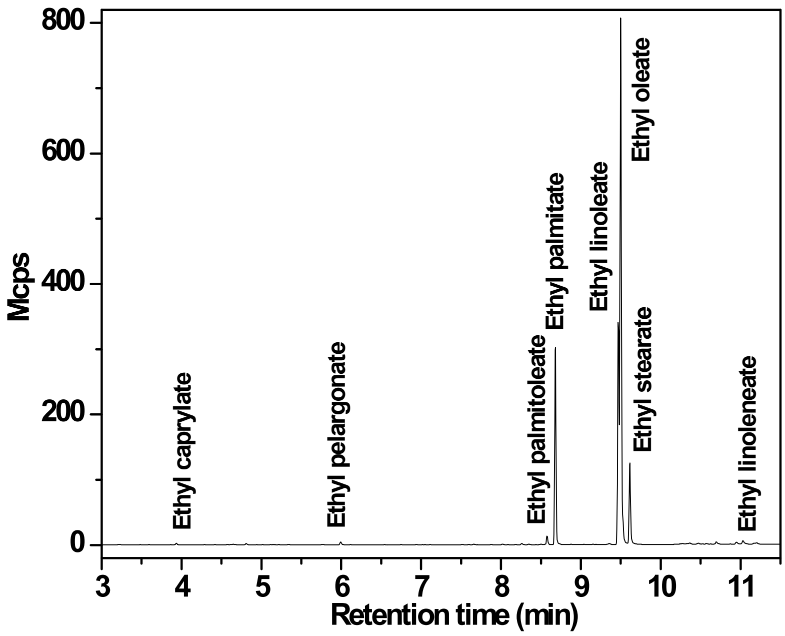

Fig. S6. Gas chromatogram of FAEE.

Table S1. The chemical analysis of the vegetable oils employed as feedstock in the present study.

Feedstock	Free fatty acid value (wt%)	Moisture content (wt%)	Saponification value (mg of KOH/g of sample)	Iodine value (mg of I_2/g of sample)
CO	0.3	0.24	181.4	88.2
WO	4.7	0.27	192.3	94.3
JO	8.8	0.36	186.2	98.2
KO	18.1	0.30	194.1	103.5

Table S2. Comparison of crystallite size of Mo/CaO at varying loadings of molybdenum and calcination temperature.

Catalyst	Crystallite size (nm)
CaO	33.0
1Mo/CaO-700	26.8
2Mo/CaO-700	26.8
3Mo/CaO-700	22.5
4Mo/CaO-700	25.2
5Mo/CaO-700	25.2
3Mo/CaO-300	33.1
3Mo/CaO-400	32.6
3Mo/CaO-500	22.8
3Mo/CaO-600	22.5
3Mo/CaO-800	21.5

References

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3. E. Li, Z. P. Xu and V. Rudolph, *Appl. Catal. B: Environ.*, 2009, **88**, 42.
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