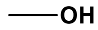
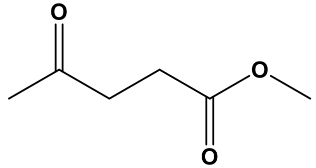
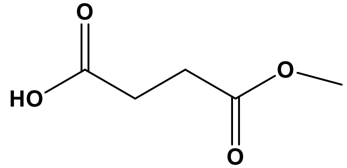
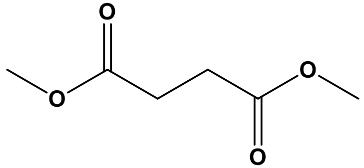
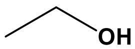
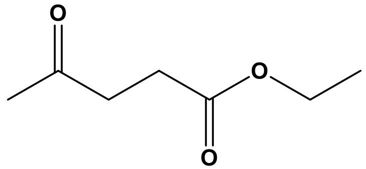
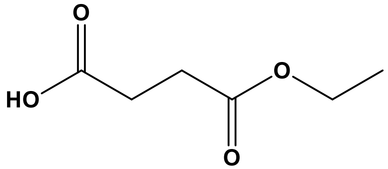
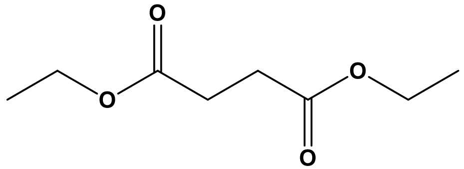
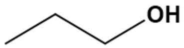
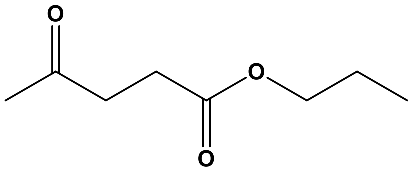
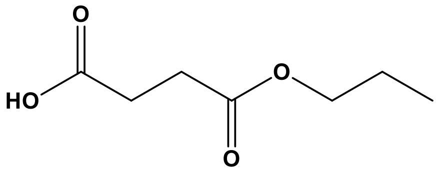
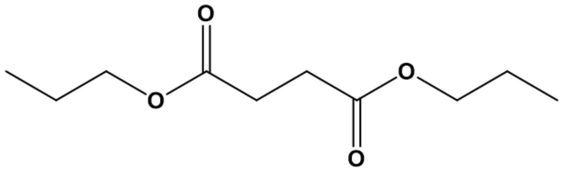
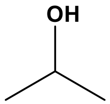
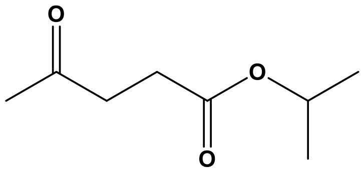
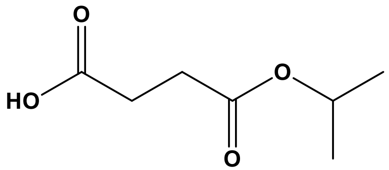
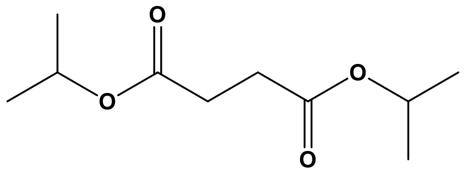
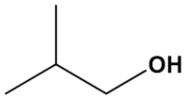
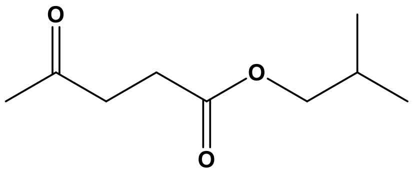
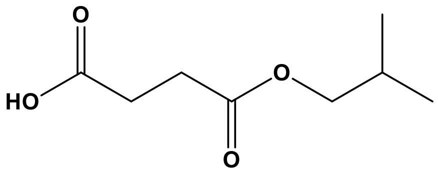
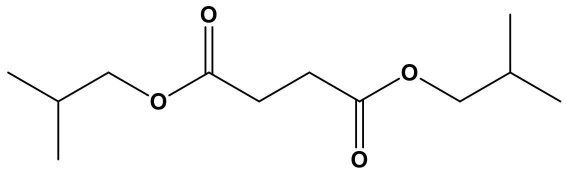
Substrate study of levulinic acid and succinic acid with different alcohols over SiW_{12}/nMCM-48

The study of different substrates holds enormous importance in developing an industrial catalytic process. The versatile nature of found best catalyst, SiW_{12}/nMCM-48 was explored for the esterification of levulinic acid and succinic acid with alcohols having varying carbon chains (unbranched and branched) (Table 1). All the reactions were carried out in the respective optimized conditions of esterification of levulinic acid and succinic acid with n-butanol.

From the results it is observed that alkyl levulinates with C1 to C8 chain alcohols were obtained with excellent yields (>75%). All the primary alcohols up to C4 chain length converts easily into their respective levulinate esters [1–3]. However, as the chain length increases or branching occurs (in case of isopropyl alcohol, isobutyl alcohol and tertbutyl alcohol), the rate of ester formation decreases due to the steric hindrance. At the same time, it is in interesting to note down that for C5-C8 alcohols, >80% and the negligible difference in the conversion rates was observed. Even though the stearic hindrance was present, this appreciable catalytic activity was achieved which may be attributed to the contribution from the electronic factors, that promote the stabilization of formed carbocation intermediates, responsible for the ester formation. Importantly, most of these levulinates esters owns outstanding fuel-blending properties and other commercial applications.

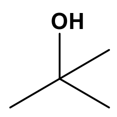
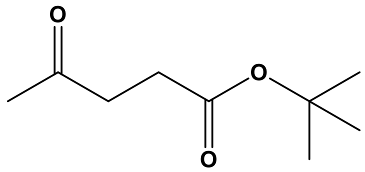
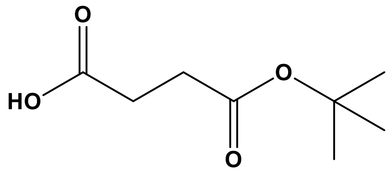
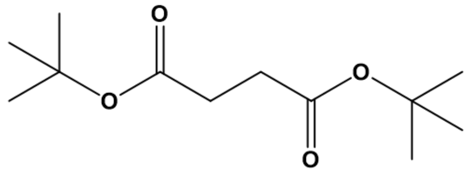
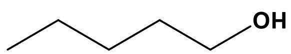
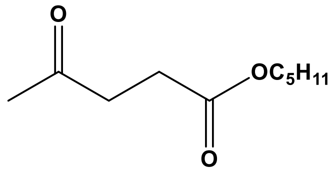
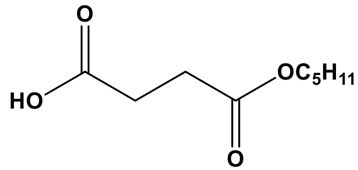
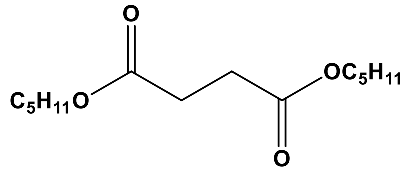
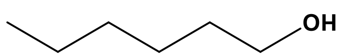
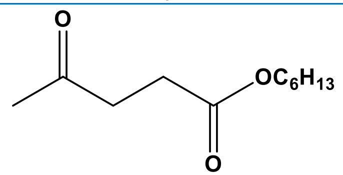
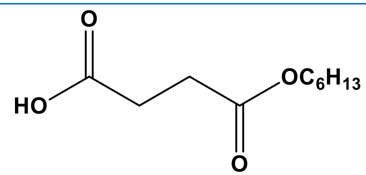
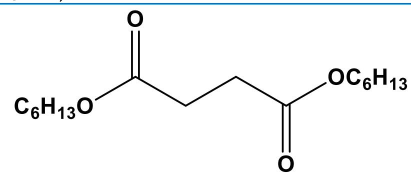
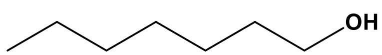
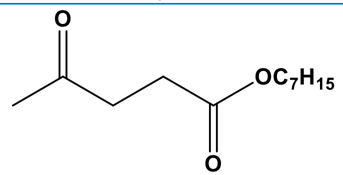
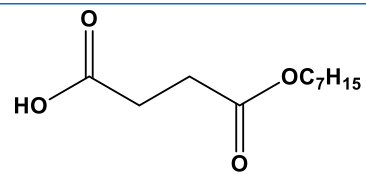
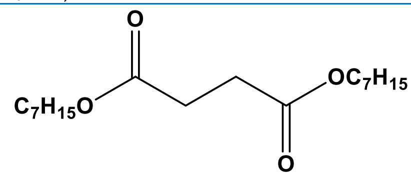
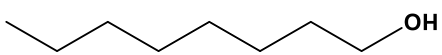
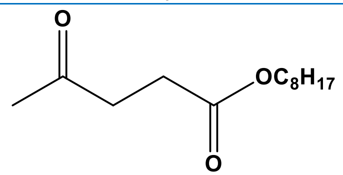
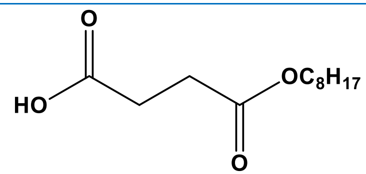
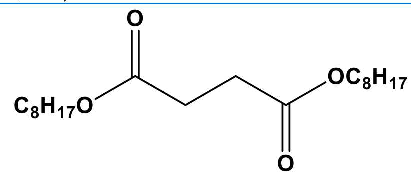
Also, appreciable conversions (>80%) and expected trend in the results were observed for the esterification of succinic acid with C1 to C8 chain alcohols. From simple one carbon chain primary alcohol to eight carbon chain, the conversion slightly due to increasing carbon chain lengths. Furthermore, when the branched chain alcohols were used, conversion decreases to as low as 16% with tertbutyl alcohol.

Table 1 Esterification of levulinic acid and succinic acid with different alcohols

Substrates	Alkyl levulinates *% **Conv**/Sel	Alkyl succinates *% **Conv**/Sel (monoester/diester)	
	 **85**/100		 **100**/(28/72)
	 **78**/100		 **91**/(42/58)
	 **77**/97		 **90**/(40/60)
	 **39**/100		 **41**(67/33)
	 **77**/98		 **87**/(47/53)

*% Conversion/selectivity of ester/s

Table 1 continued…on next page

Substrates	Alkyl levulinates *% **Conv**/Sel	Alkyl succinates *% **Conv**/Sel (monoester/diester)	
	 **21**/100		 **16**/(93/07)
	 **87**/99		 **92**/(39/61)
	 **85**/100		 **91**/(32/68)
	 **84**/99		 **90**/(26/74)
	 **83**/100		 **85**/(12/88)

*% Conversion/selectivity of ester

Notably, one thing is certain that steric hindrance plays a vital role in esterification reaction [4]. As we go on indulging long chain or branched alcohols, a little bit of low reactivity was observed compared to their respective simpler alcohols. Nevertheless, the superiority of the catalyst lies in the progress of each substrate to yield the desired products.

Thus, the substrate study with different alcohols offers versatile aura for synthesizing the top value added products.

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