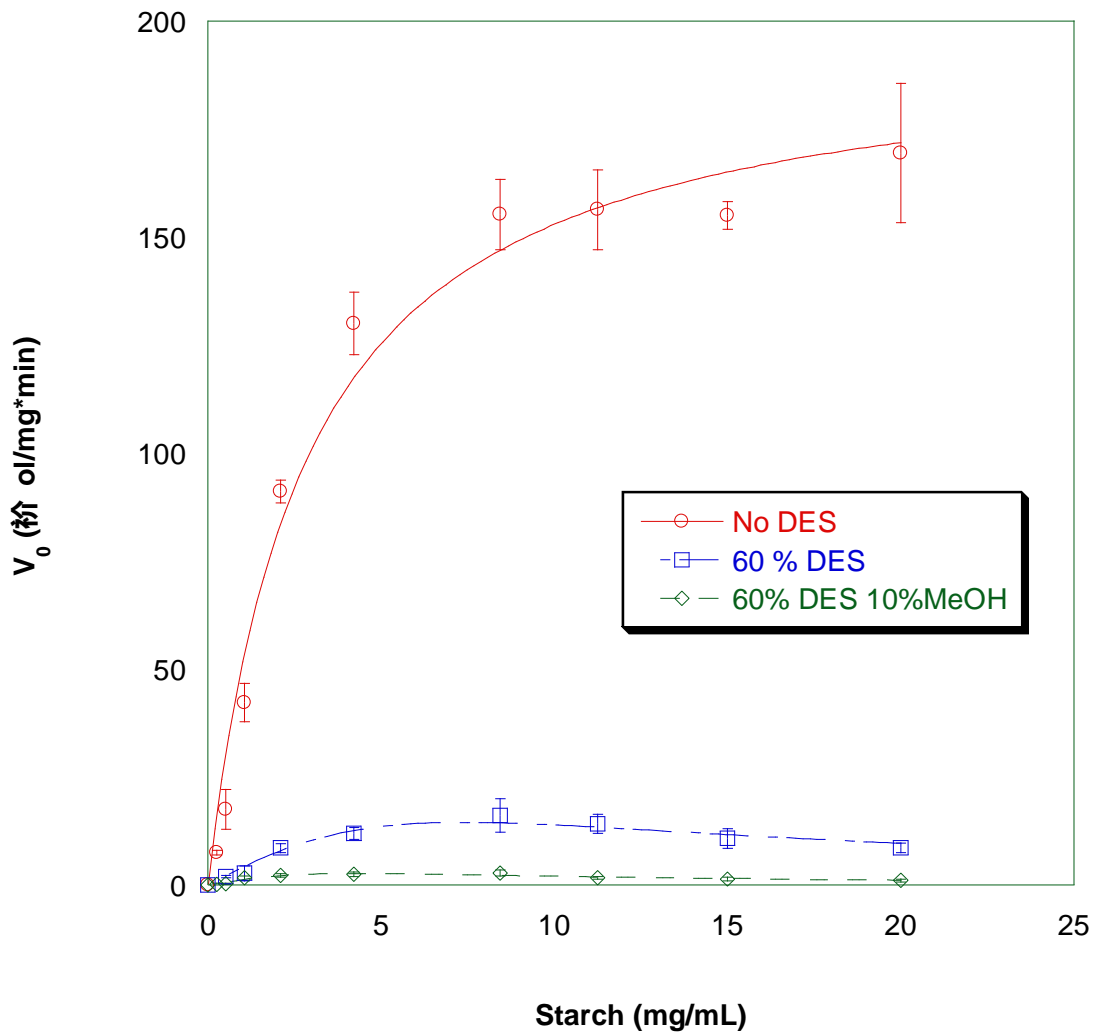


## Supplementary Information

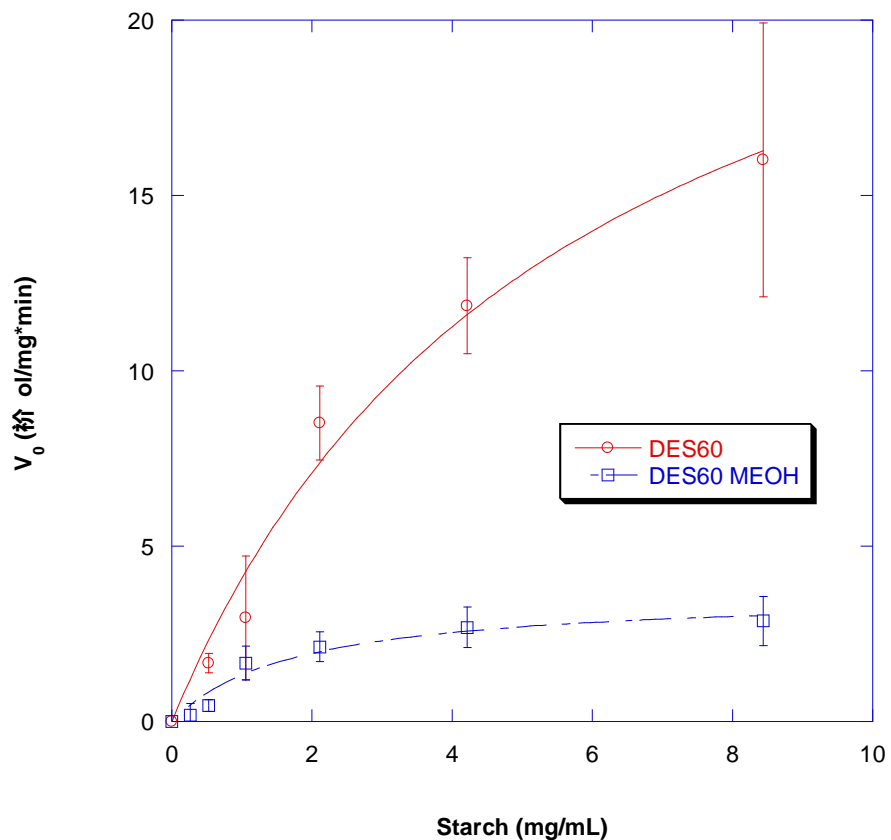
**Table S1.** Deep eutectic solvents prepared in this work.

#	DES	Mol ratio <sup>1</sup>	T <sub>m</sub> °C <sup>1</sup>	Method of preparation <sup>1</sup>
<b>Amides</b>				
1	Choline chloride : urea	1 : 2	12	Heating under vacuum
2	Choline chloride : methyl urea	1 : 2	29	Heating under vacuum
<b>Acids</b>				
3	Choline chloride : malonic acid	1 : 1	10	Heating
4	Choline chloride : levulinic acid	1 : 2	RT	Heating
<b>Alcohols</b>				
5	Choline chloride : ethylene glycol	1 : 2	-10	Heating
6	Choline chloride : D-isosorbide	1 : 2	RT	Heating
7	Methytriphenylphosphoniumbromid : glycerol	1 : 2	26	Heating
8	Choline chloride : glycerol	1 : 3 o 1 : 2	-20	Heating
9	Choline chloride : benzyl alcohol	1 : 2	RT	Heating
<b>Natural DES (NADES)</b>				
10	Choline chloride : 1,3-propanediol : water	1 : 1 : 1	-110	Heating up to 50 °C (no vacuum)
11	Choline chloride : sucrose : H <sub>2</sub> O	4 : 1 : 4	-83	Heating
12	Choline chloride : glucose : H <sub>2</sub> O	5 : 2 : 5	-84	Heating

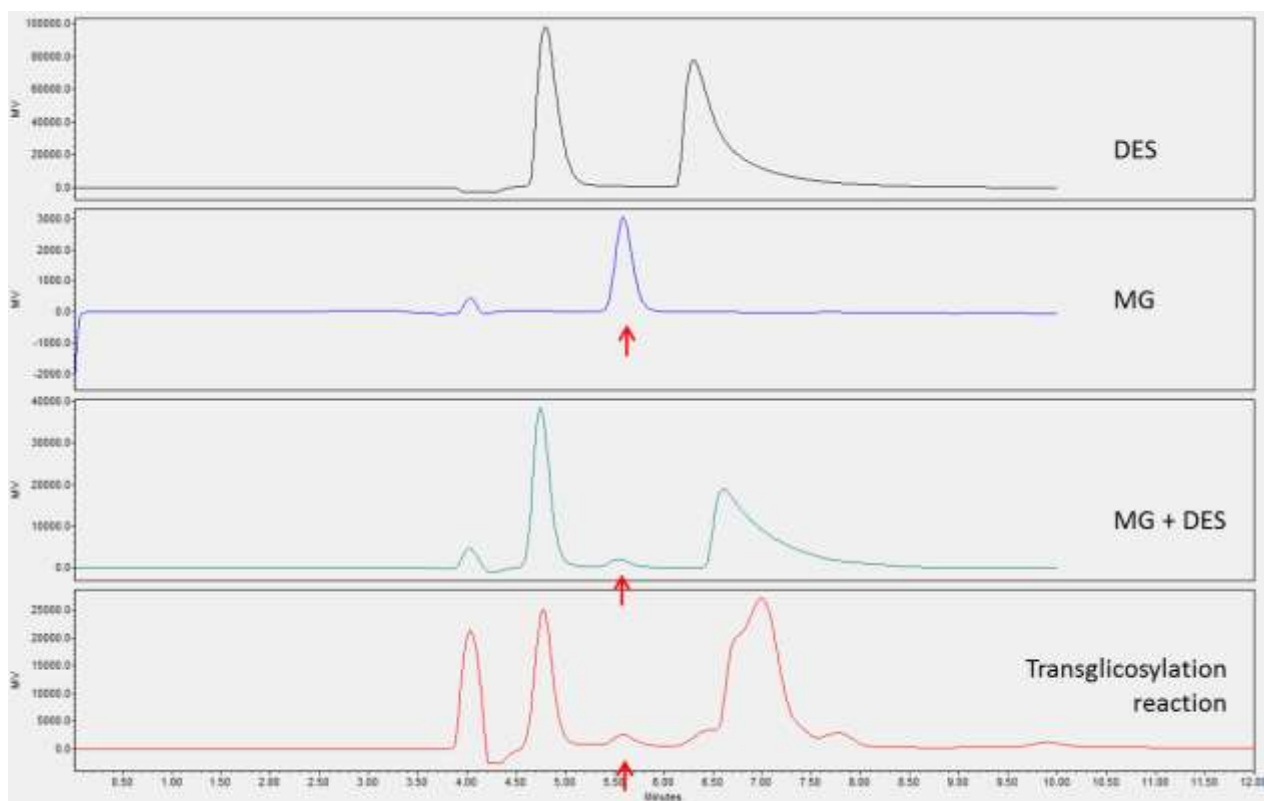
<sup>1</sup>The molar ratio is given as well as the melting point of the eutectic mixture if known. The solvents were prepared by the method indicated.



**Figure S1.** Non-linear curve fitting to Michaelis-Menten or inhibition product equations. Initial velocities ( $\mu\text{mol/mg}\cdot\text{min}$ ) were plotted against increasing concentrations of starch ( $\text{mg/mL}$ ). In the case of the reactions carried out in DES, viscosity became a limiting factor at high starch concentrations. Error bars correspond to standard deviation of triplicates.



**Figure S2.** Initial velocities vs Starch concentration in DES and DES:MeOH medium. Since viscosity became a limiting factor, data at starch concentrations above 8  $\text{mg}/\text{mL}$  were discarded, and the remaining data were fit to the Michaelis-Menten equation. Error bars correspond to standard deviation of triplicates.



**Figure S3.** Chromatographic profile of standards and alcoholysis reaction products. In black, 80% DES; in blue, methyl glucoside (MG) directly dissolved in mobile phase (ACN:H<sub>2</sub>O, 80:20); in dark green, MG dissolved in 40% DES; in red, alcoholysis reaction products (includes a mixture of dextrans, glucose, methanol, DES and MG). Samples from reactions were previously diluted 1:1 with buffer and digested for 6 h with glucoamilase from *A. niger* to hydrolyze remaining amylose. After digestion, samples were filter through a 0.22  $\mu$ m nylon membrane and injected into a Gold-amino column. The red arrow shows the peak corresponding to the product of interest MG to be quantified.