The use of UNIQUAC equation

In a particular process ethanol needed to be partly removed, by evaporation, from a mixture of ethanol and biodiesel (4 wt-% ethanol). The Biodiesel was modeled as an ester $C_{17}H_{35}$-COO-CH_3. The first step of calculation required an estimation of the normal boiling point (NPB) of the mixture. No data was available , so initially an ideal mixture was assumed. This yielded the normal boiling point of ~ 124°C. In ideal case, no interactions between the molecules are taken into account, hence a more accurate estimate was sought.

The obvious candidate was the UNIQUAC equation, which has a well-proven activity coefficient model. This yielded the normal boiling point of ~ 142°C. Most engineers would have taken this value as good enough. Are the results trustworthy?

No, as no experimental data was available, the binary parameters have been set to zero within the code. As a result the combinatorial part gives negative deviations from Raoult's law, resulting in a higher NBP.

The use of Modified UNIFAC with the NRTL parameters, which takes into account both the interactions between the molecules and the combinatorial part, results in the normal boiling point dropping down to 108°C. This was later confirmed experimentally.

As a consequence, the use of the UNIQUAC equation was forbidden in that particular company!