

## Determination of Critical Properties for Reactive Mixtures: Hydrodesulfurization of 4, 6-Dimethyldibenzothiophene

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A computational procedure to determine the critical points of a reactive mixture in the hydrodesulfurization of 4, 6-dimethyldibenzothiophene (4, 6-*DiMeDBT*) with tetralin as a solvent, has been developed. The critical point for a mixture of specified composition is the set of conditions (e.g. T and P) at which the mixture and the equilibrium phase have identical composition and density. Therefore, for reacting mixtures undergoing a kinetically controlled reaction process, points on the phase boundary at “close to critical” conditions are characterized by nearly identical phase compositions and phase densities. The hydrodesulfurization of 4, 6-dimethyldibenzothiophene reaction is carried out in a reactive batch distillation process. The thermodynamic analysis considers the simultaneous calculation of the reactive and non-reactive residue curve maps (Viveros-García et al., 2006) and the critical points are obtained using the Heidemann and Khalil method (Heidemann and Khalil, 1981).

Keywords: critical point, HDS, reactive distillation

### 1. Extended Abstract

The computation of the critical points is carried out through the algorithm shown in Figure 1. To compute the non-reactive and reactive residue curves, an initial point close to the left corner on the triangular diagram was chosen. This initial point represents the composition of a “sulfured” diesel with mole fractions: 0.0005 for *DBT* or 4, 6-*DiMeDBT* (**AB**), 0.005 for H<sub>2</sub> (**C**) and 0.9945 for Tetraline (**D**), and it is assumed that no reaction products are present. These initial mole fractions correspond to the following *element* fractions:  $W_A^{0*} = W_B^{0*} = 9.695 \times 10^{-4}$ ;  $W_C^{0*} = 3.393 \times 10^{-2}$ ;  $W_D^{0*} = 0.96413$  and their normalization (considering constant  $W_D^{0*} = 0.96413$ ) gives:  $W_A^0 = W_B^0 = 0.02703$ ;  $W_C^0 = 0.94594$ . These normalized *element* fractions allow to locate the initial point in the element phase diagram near to the **C** node (pure H<sub>2</sub>). Also values for the operating pressure and the reaction-separation parameter  $\alpha$  must be given according to the Figure 1.

With the above specifications a bubble point temperature calculation is performed and the corresponding element fractions are evaluated. After that, a testing step over the liquid and vapor composition vectors is performed. If the composition differences are

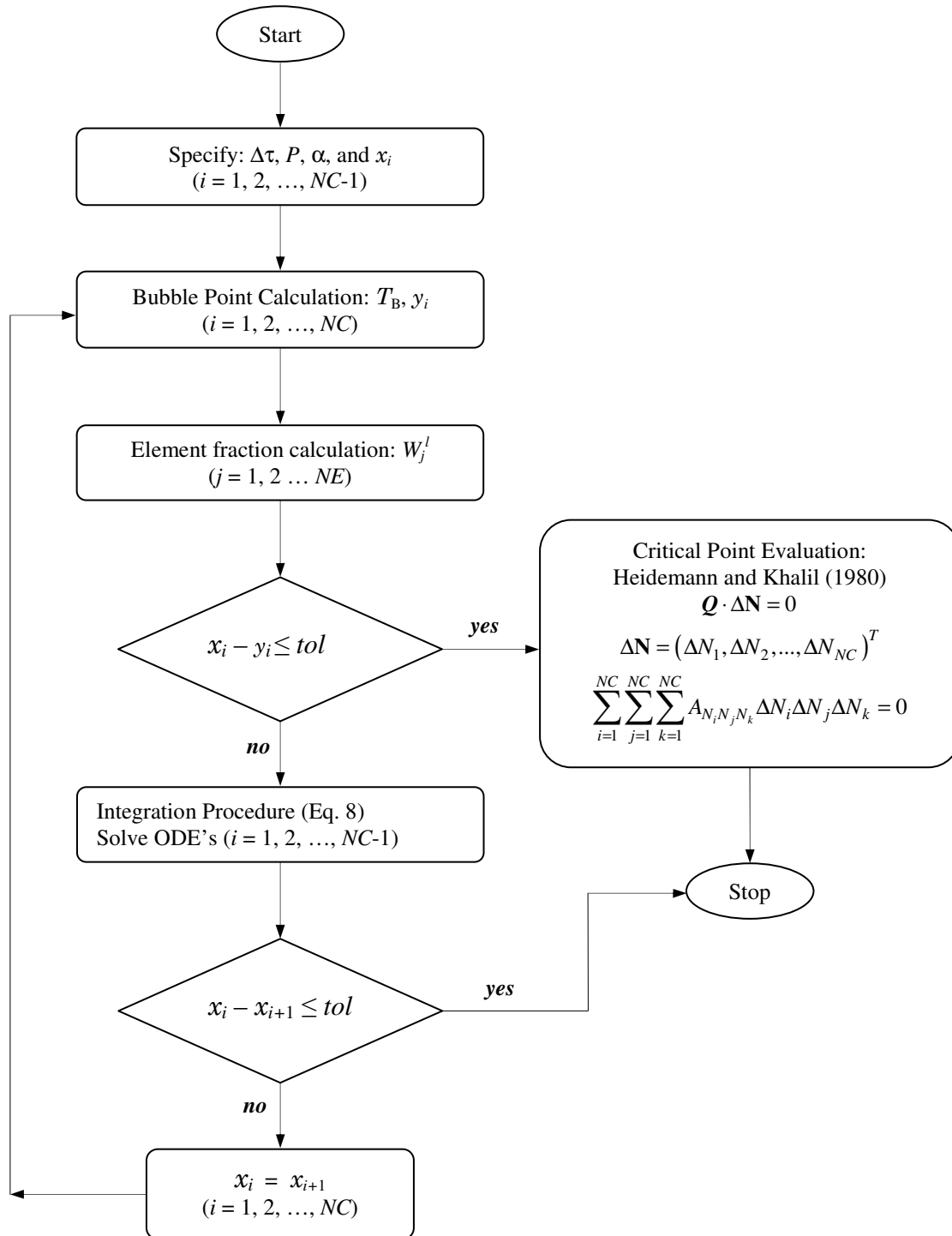


Figure 1 Algorithm for Critical Points Calculation of a Reacting Mixture

smaller than a tolerance ( $tol = 1E-10$ ), then a critical point evaluation through the Heidemann and Khalil method is verified. According to the methodology proposed, several simulations at different operating pressures (10, 15, 20, 25 and 30 atm) were done. At  $P = 30$  atm several critical points for the reactive mixtures were identified, as can be observed in Figure 2. On the other hand, it can be observed in Figure 2 that, for values of  $\alpha \leq 10$ , all curves point to a binary critical point in terms of *elements*. If the  $\alpha$  value is augmented ( $\alpha = 90$ ) the reactive residue curve moves close to the 3-MeCHT reaction product, and it ends at another critical point. Therefore, in absence of hydrogen in the liquid phase ( $AC_4$  node, in Figure 2), the increment of catalyst loading, leads the reactive system to critical conditions, where the distinction between the phases is not possible. In this way, at  $P = 30$  atm, the temperature region as well as the catalyst loading should be carefully considered for the design of a reactive section in a reactive distillation column, due to the critical points presence.

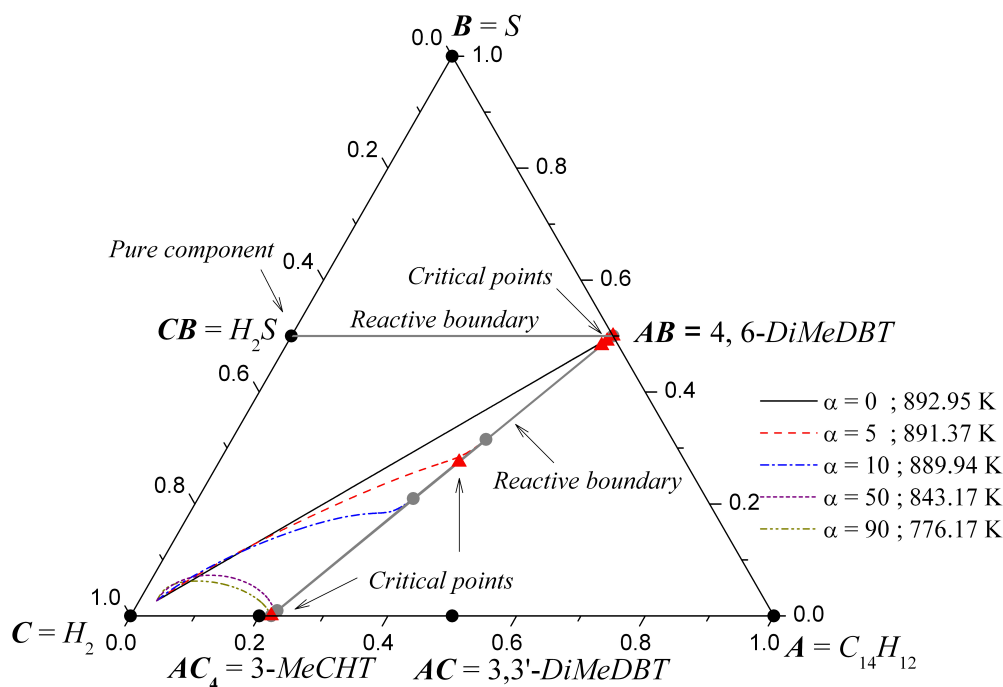


Figure 2. Location of critical points for the HDS for 4, 6-DiMeDBR reactive system at  $P = 30$  atm

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