

## Ternary Phase Diagram Biodiesel Fuel – Methanol – Water

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In the publications [1] and [2] the ternary phase diagram Biodiesel (B)–Methanol (M)–Glycerol was described. During the experiments the strong influence of small amounts ( $\leq 0,025$  weight %) of water (V) on this equilibrium was found out. Whilst B is miscible with waterfree M in every ratio up to the normal boiling point of M (64,7 °C), B and V are at room temperature practically unmiscible [3].

This work deals with the phase equilibria in the mixture of B, M and V in the temperature range 25–65 °C. The resulting ternary phase diagram B–M–V may help to elucidate more the role of water in the production process of B *via* transesterification of natural oils and fats by methanol.

### Experimental

The creation of the ternary phase diagram B–M–V consisted of two steps: measuring of equilibrium binodal curves and determination of tie lines (conodes).

#### *Binodal curves*

A homogeneous mixture of two of these three 3 components with suitable composition and temperature 25 °C was titrated (micropipette, smallest dose 200  $\mu$ l, accuracy  $\pm 1\%$ ) by the third component to the origin of the turbid system. The homogeneity of the mixture was checked by measuring of its transmittance  $\tau = 100 \cdot I(\lambda) / I_0(\lambda)$  (%).  $I_0(\lambda)$  and  $I(\lambda)$  are flows of light with wavelength  $\lambda$  incident and coming out of the measuring glass cell (volume 30 cm<sup>3</sup>, light path 2 cm). The cell was supplied with a gastight cover with three openings for mixer, thermometer and feeding of titrant and was tempered in a special copper duplicated mantle connected with a thermostat ( $\pm 0,1$  °C). The mantle had two openings for  $I_0(\lambda)$  and  $I(\lambda)$  and was (together with the cell) a part of the spectrophotometer SPECOL 11 (Zeiss Jena, Germany) in which  $\tau$  (600 nm) was measured. The wavelength 600 nm was chosen because of the minimum of absorbance of the yellow coloured B. So, for a homogeneous initial mixture,  $\tau$  was always 100%. As the document of the first inhomogeneity of the system the fall of  $\tau$  value from 100 to 99% was considered.

After reaching the turbid system at the lowest chosen temperature 25 °C, the temperature was increased to 5 °C.

The mixture became homogeneous again and could be again titrated by the same component to the origin of new inhomogeneity. So in one experiment a series of 9 points for 9 binodal curves at 9 various temperatures (25, 30, 35, 40, 45, 50, 55, 60, 65 °C) and at atmospheric pressure were obtained. This method was repeated for various initial compositions of suitable two component systems (12 of B + M, 7 of M + V) and for pure components B (titrated by V) and V (titrated by B).

These experiments spent a lot of time; measuring of 1 point on the binodal curve at the given temperature (threetimes) lasted more than 2 hours.

#### *Tie lines*

A mixture of B, M and V of exactly known composition from the heterogeneous part of the diagram at chosen temperature was prepared. This mixture was intensively mixed at this temperature 3–4 hours. Then the mixing was finished, but the chosen temperature was still kept. The heterogeneous mixture was left (mostly over night) to form two equilibrium three component homogeneous mixtures, which were analysed. Their compositions determined the intersections of the given tie line with the binodal curve.

The apparatus used was a glass, gastightly closed double jacketed vessel (volume 75 cm<sup>3</sup>) connected with the thermostat. It was supplied with two openings in the cover (for thermometer and feeding the heterogeneous three-component mixture) and one opening in the lower third of the side wall (to get the samples of both equilibrium phases after piercing the polypropene stopper by a syringe needle). The precise mixing of the heterogeneous system was made sure by electro-magnetic stirrer.

### Determination of Composition of Equilibrium Phases

#### *Methanol*

M was determined by the GC method on the czech device CHROM 5. The column (length 120 cm, diameter 0.3 cm, filled with PORAPAC Q, temperature 130 °C) and the detector FID (temperature 130 °C) were used. The temperature of the

sampler was 265 °C, flow of the carrier gas He was 3 cm<sup>3</sup>/5 s, of H<sub>2</sub> 30 cm<sup>3</sup>/min and of air 450 cm<sup>3</sup>/min. The retention time of the peak of M increased from 1.2 to 1.5 min with its decreasing concentration. For the injection of samples the Hamilton syring 0.01 cm<sup>3</sup> was used.

**Method:** First of all the concentration of M in % by weight (w%) in the sample ( $c_M$ ) was estimated by comparing the areas of the peaks of 1 µl of pure M and sample (knowing their densities). If the estimated  $c_M \leq 10$  w%, the exact value of  $c_M$  was determined by the method of internal standards. From every sample (of known density) four solutions with known  $c_M$  of pure M and with known densities were prepared. 1 µl of the sample and of every of these four solutions were injected in the GC apparatus and the areas of the peaks of M were measured. Then the plot area –  $c_M$  was constructed. This calibration curve was linear and from its intercept on the negative side of the  $c_M$  axis the concentration of M in the sample was obtained. If the estimated  $c_M > 10$  w%, the exact value of  $c_M$  was calculated from the calibration line: areas of the peak of M in 1 µl of the calibration solutions of M in B –  $c_M$  of these calibration solutions. 1 µl of each sample of known density was injected, the peak of M measured and compared with the calibration line. The precision of both types of M determination was  $\pm 0.1$  w%.

#### Water

The concentration of water  $c_V$  (w%) was determined also by the GC method on the apparatus CHROM 5. A column (length 120 cm, diameter 0.3 cm, filled with PORAPAC N (temperature 114 °C) and the detector TCD (temperature 200 °C) were used. The temperature of the sampler was 265 °C, the flow of the carrier gas He was 3 cm<sup>3</sup>/5 s. The retention time of the peak of V increased from 0.5 to 0.8 min with decreasing concentration. The samples were injected by the same type of syringe and the method of initial estimation and exact determination of  $c_V$  was the same as in the case of M. The precision was  $\pm 1$  rel.%.

#### Biodiesel fuel

The concentration of B ( $c_B$ ) was measured as w% of methyl-esters of all fatty acids present in B. Two independent methods (GC and HPLC) were used for every sample. The difference between the results from these two methods was never greater than 1 w%. Therefore the arithmetic average of values from GC and HPLC determinations was taken as the final result. The precision of both methods was  $\pm 0,5$  w%. The mentioned GC and HPLC methods are described in detail in [3].

## Chemicals

#### Biodiesel fuel

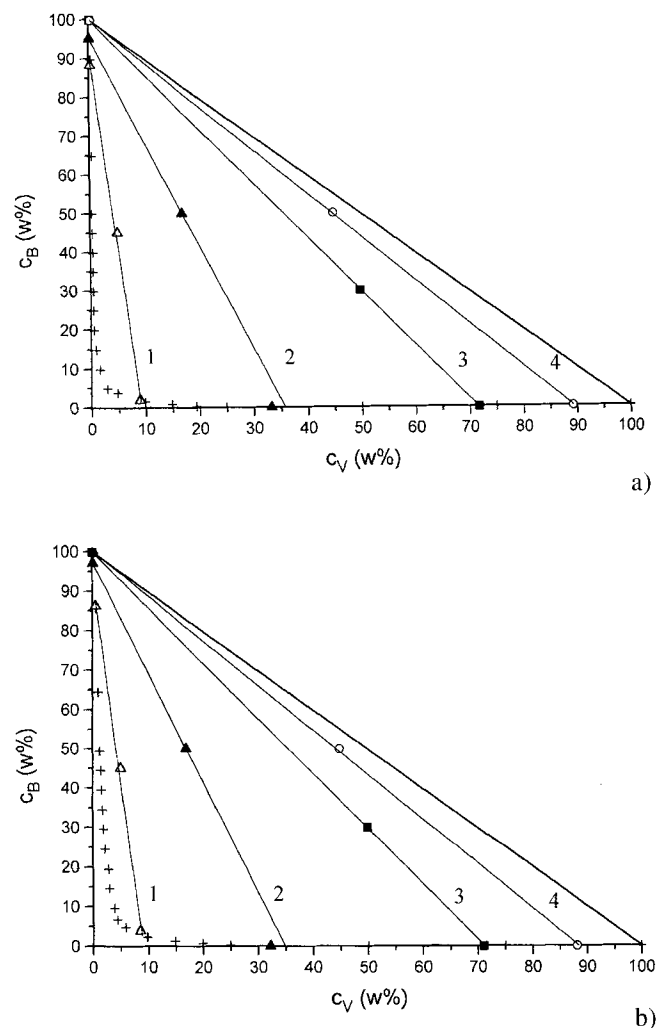
Product of the privat firm ZIEBIGER (Lužany near Jičín, Czech Republic) from rape seed oil by the method patented in [4]. Properties: density (20 °C) 0.877 g·cm<sup>-3</sup>; kinematic viscosity (20 °C) 7.16 mm<sup>2</sup>·s<sup>-1</sup>, freezing point – 12 °C, flash point 90 °C, Conradson carbonisation index (100%) 0,022 w%, neutralisation number 0.17 mg KOH g<sup>-1</sup>; concentrations: rape seed oil (HPLC) 0,85 w%; methyl-esters of fatty acids of rape seed oil 98.1 w% (HPLC), 98.0 w% (GC); potassium 0.5 mg·dm<sup>-3</sup>, calcium 6 mg·dm<sup>-3</sup>.

#### Methanol

Quality p.a. from the firm LACHEMA Brno, Czech Republic with 0,269 w% of water (determined by GC).

## Results

The figures 1a,b show examples of the complete triangular ternary phase diagram B–M–V at temperatures 25 and 45 °C. In every of these diagrams four tie lines experimentally determined are introduced. Coordinates of all tie lines are given



**Fig. 1a, b** Ternary phase diagram biodiesel (B)–methanol (M) – water (V) at 25 °C (fig. 1a) and 45 °C (fig. 1b). Experimental points of the binodal curve are marked by +. 1, 2, 3 and 4 are experimental tie lines.  $c_B$  and  $c_V$  are in w% of B and V. For  $c_B = c_V = 0$  is  $c_M = 100$  w%.

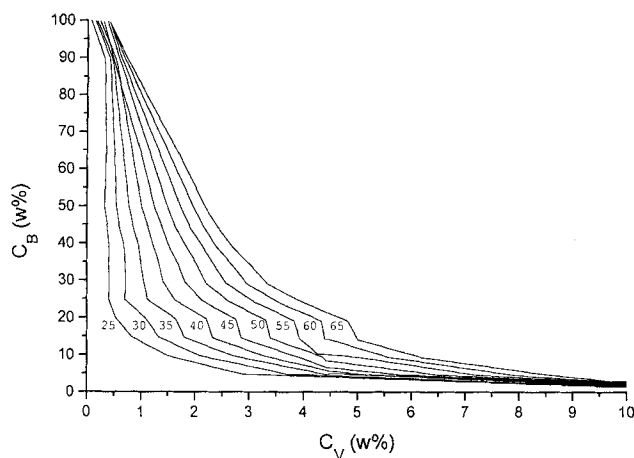
in Table 1. The main and most interesting parts of all binodal curves measured at temperatures 25, 30, 35, 40, 45, 50, 55, 60 and 65 °C are introduced in fig. 2. Higher temperatures would request an apparatus for higher than normal pressure.

**Table 1** Experimental coordinates of tie lines in fig. 1a,b . All concentrations given in w%. Row 1 (temperature 25 °C, tie line nr.1, fig.1a) ; 2 (25 °C, 2, 1a) ; 3 (25 °C, 3, 1a) ; 4 (25 °C, 4, 1a) ; 5 (45 °C, 1, 1b) ; 6 (45 °C, 2, 1b) ; 7 (45 °C, 3, 1b) ; 8 (45 °C, 4, 1b)

Row	Biodiesel			Methanol in the system			Water		
	initial	upper	lower	initial	upper	lower	initial	upper	lower
1	45	2.0	88.3	50	88.3	11.5	5	8.9	0.18
2	50	95.1	0.0	33	4.8	65.8	17	0.05	33.2
3	30	99.9	0.0	20	0.0	24.8	50	0.9	71.1
4	50	99.8	0.0	5	0.0	8.8	45	0.2	89.2
5	45	39.0	86.2	50	88.3	13.3	5	7.5	0.5
6	50	97.1	0.0	33	2.8	64.9	17	0.05	32.2
7	30	99.8	0.0	20	0.1	23.9	50	0.05	71.1
8	50	99.8	0.0	5	0.1	11.9	45	0.07	88.1

## Discussion

The form of the isothermal - isobaric diagrams B–M–V in the temperature range 25–65 °C and by normal pressure is dictated mainly by the mutual solubility of the pairs of the substances used. V and M as like as B and M (waterless) form one phase



**Fig. 2** Main part of the ternary phase diagram B–M–V–temperature in the interval 25–65 °C. Breaks on individual binodal isotherms characterize the experimentally found compositions of boundary mixtures.  $c_B$  and  $c_V$  are in w% of B and V.

in every ratio. B and V are practically immiscible even by 65 °C (0.07 and 0.41 w% of V in B by 25 and 65 °C). Therefore all determined binodal curves – isotherms have in the diagram the form of asymmetric hyperboles with asymptotes tending to the points 100% of B and V. The area of maximum homogeneity of the three-component mixtures is situated of course near the point 100% M. But the contents of B and V in M are not greater than 15 and 1 w% by 25 °C and 25 and 4 w% by 65 °C (see fig. 2).

From fig. 2 follows also an interesting small deformation of all measured binodal curves of mixtures with 15–20 w% of B. This deformation is shifted with increasing temperature to higher contents of V. All tie lines have practically the same

shape (see fig. 1a,b). They form in every isothermal – isobaric diagram a fan of lines. One of their final points lies very close to the corner 100% B, the second one on the opposite part of the binodale near the axis M–V. The experimentally determined tie lines (see fig. 1a,b) for 25 and 45 °C were constructed with the help of three points. The composition of the inner point (initial heterogeneous system) was chosen, the compositions of both ending points (homogeneous equilibrium systems) was found out by determination of all three components. In all cases these three points fulfil a linear dependence with the correlation coefficient > 0.999. This result confirms also the validity of decreasing the  $\tau$  (600nm) value from 100 to 99% as the criterion of the first inhomogeneity in the system (see experimental part). Only tie lines no. 2 make an exception. The shape of these lines clearly does not agree with the point on the axis  $c_V$ . Because of no doubt about the positions of the internal and the second final point, this third point was not respected in the construction of these two tie lines. The authors are not yet sure if this disproportion is in the analysis of these mixtures (repeated several times with the same result) or has some other reason.

## References

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