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Theoretical and experimental study of monoethanolamides and diethanolamides as potential additives to fossil diesel fuel

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Abstract: In this work, theoretical and experimental study of monoethanolamides (MEAD) and diethanolamides (DEAD) is presented. The aim was to investigate the thermodynamics of addition reactions used in the synthesis of MEAD and DEAD. The reactions have exothermic character and alkyl elongation affects the reaction enthalpy of DEAD production reactions. In the experimental part, the prepared MEAD and DEAD samples were preliminary tested as a potential additive in diesel fuel. The research focused on measuring three key properties: i.e., foaming, lubricity, and cetane number. The results suggest that MEAD is a suitable additive for diesel fuel.

Keywords: green chemistry, DFT, thermodynamics, eco-friendly additive, foaming, corrosivity

Introduction

Detergents are a group of surfactant molecules with an amphibole structure, where the long tail has a non-polar part and the other side has a short polar part. Alkanolamides may be considered such substances, exhibiting various interesting properties, which consist of a long non-polar alkyl chain and a polar amide moiety. While most surfactants increase the degree of corrosion, the diethanolamide solution protects both steel and iron from corrosion (Sanders, 1958). These substances also have anticorrosive properties, antifoaming properties, and they increase lubricity and cetane number of fuels (EP 1 227 143). One way to improve fuel economy of an engine and reduce fuel consumption is to reduce engine friction. Currently, fatty acid esters, fatty acid amides, and fatty acid esteramides are applied as environmentally friendly friction modifiers (Hui, 1998).

As it is reported in literature (Gaurav et al., 2017; Liu et al., 2021), alkanolamides can be prepared from various raw materials, e.g., FFA (free fatty acids), TAG (triacylglycerols), FAME (methyl ester of fatty acids), alkanolamines, i.e., monoethanolamine (MEA) or diethanolamine (DEA). Despite the wide variety of alkanolamides, monoethanolamides (MEAD) and diethanolamides (DEAD) are of particular interest in technical practice (Shahidi, 2005). An additive on this basis can potentially be added to any type of organic fuel (gasoline, diesel, FAME, ethanol) or to mixtures thereof. In general, optimum concentration of an additive is reported to be 1 to 5 % v/v relative to pure fuel (Kleinová, Cvengrošová and Cvengroš, 2013; Mikulec et al., 2010). In case of solutions with anhydrous ethanol or even with water, DEAD and MEAD have an emulsifying effect as they form a stable microemulsion. The presence of a nitrogen component in diesel, for example added urea, leads to in better combustion with lower CO, Nox, and solid particle emissions. This also results in lower fuel consumption. Therefore, ethanolamine or diethanolamine, from the production of MEAD or DEAD, need not be removed as an unreacted reactant from the mixture after amidation.

On the other hand, optimal adjustment of the concentration ratios of additives and fossil fuel with respect to different physicochemical properties is investigated. Considering the work published so far, the objective of this study is to investigate the thermodynamics of reactions occurring in the synthesis of MEAD and DEAD from fatty acids. In the experimental part, MEAD and DEAD samples were prepared by internal synthetical treatment and purification technics according to Pokorný and Dubská (1986). Consequently, these samples were tested as additives in diesel fuel. This part of research focused on three key properties i.e., foaming, lubricity and cetane number.

Materials and Methods

Samples preparation

Condensation reaction of MEA (Lachema, Brno) with technical oleic acid (Lachema, Brno) was used to prepare the MEAD sample. Acid number of oleic acid was 196.0 mg (KOH)/g and the declared acid abundances (acyl profile) were as follows: C16:0-9.8; C18:0-2.9; C18:1-61.2; C18:2-23.0; C18:3-2.2;

C20:0-1.0 (area percentages by GLC chromatogram).

To limit the formation of ester to a minimum, a slight molar excess of alkanolamine to fatty acids is usually used (1.02:1 to 1.10:1) at the working temperature for MEA, which is around its boiling point of 170 °C. Both reaction components are mixed at 80 °C to 120 °C. The reaction mixture is heated up to 160—170 °C. During the reaction, water is removed and the acid number decreases. Continuous analysis of the reaction mixtures was not performed, only the final products of the reaction were determined.

The reaction can be considered complete when the acid number drops to 5 mg KOH/g or lower. The excess MEA is distilled off under reduced pressure, at the yield of above 90 %. The reaction time of 4 h was determined according to Pokorný and Dubská (1986). The ratio of reactants was 1.1:1 (alkanolamine:FFA). As suggested in Scheme 1, up to three product species (**3/MEAD**, **4** and **5**) with supposed yields are considered to be formed in this type of reaction (Pokorný and Dubská, 1986). The reaction was carried out without a catalyst under constant stirring at significantly reduced pressure of 2 kPa at 160 °C. During the reaction, the decrease in the acid number was monitored, when the acid number did not decrease significantly any further, the reaction was considered complete. The final acid number was 0.7 mg KOH/g. The sample was finally purified by distillation on a molecular evaporator at 220 °C and 30 Pa. The resulting product was a distillate with the acid number of 0.9 mg KOH/g. The obtained product was solid at room temperature and insoluble in water.

Diethanolamides were prepared in a similar manner as MEAD according to Scheme 1 (see product **8/DEAD**). DEAD are produced by reacting FFA or FAME with DEA in a molar ratio of 1:2 at 150—170 °C. During the reaction, water or MeOH is removed and the acid number decreases. When the acid number drops to 5 mg KOH/g or lower, the reaction is considered to be complete (Hui, 1998).

The molar ratio of reactants was 2:1 (alkanolamine:FFA) and the reaction temperature was 150 °C at 2 kPa. The whole synthesis needed 150 minutes to complete. The sample was finally processed on a molecular evaporator at 180 °C and 20 Pa so that the front part was evaporated and the distillation residue was the product. The obtained DEAD had an acid number of 0.3 mg KOH/g and it was obtained as viscous liquid soluble in water.

To test the prepared compounds as additives, neat diesel fuel obtained from VÚRUP, Bratislava was used; the corresponding basic physicochemical properties are summarised in Tab. 1. This diesel fuel was mixed with synthesised MEAD and DEAD samples at 0.2, 0.5, 0.8, 1.4 and 2.0 wt. %, respectively. Homogenisation of the mixtures was carried out under constant stirring and at elevated temperature (40 °C).

Physicochemical measurement

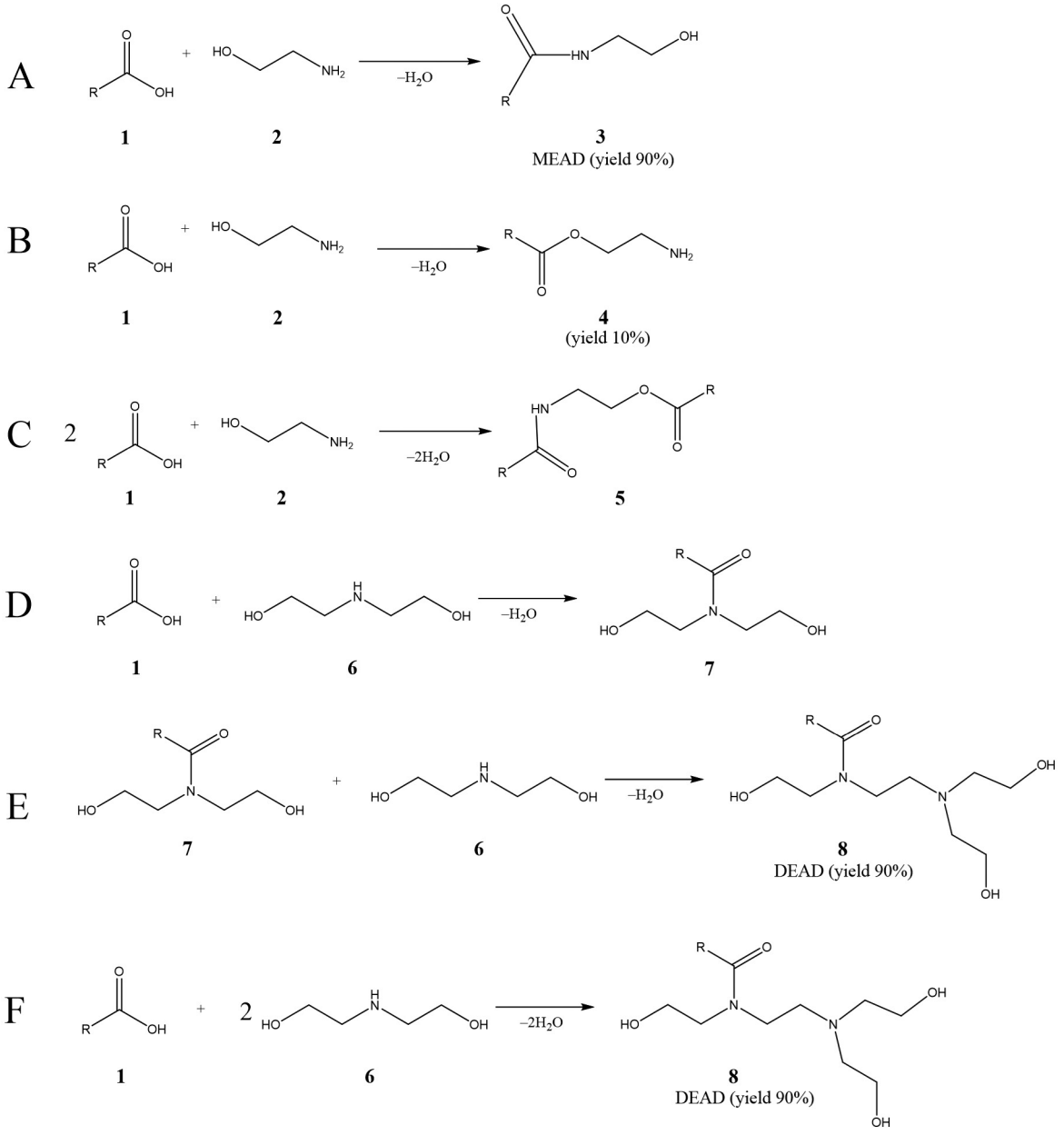
The prepared samples of MEAD and DEAD were tested as foam reducing additives, lubricity additives, and cetane number enhancers. The physicochemical

Tab. 2. Test methods and standards used to measure MEAD and DEAD samples.

Property	Applied test method
Foaming of diesel fuel	AFNOR NF MO-075
Lubricity	STN EN ISO 12156-1
Cetane number	STN EN ISO 5165
Acid number	STN EN ISO 660

Tab. 1. Physicochemical properties of nonadditive diesel fuel used for testing.

Property			
Density at 15 °C, kg/m^3	840.5	Distillation temperatures, °C	
Viscosity at 40 °C, mm^2/s	2.681	start of distillation	198.8
Sulphur content, mg/kg	6.2	10 vol. %	222.6
Cetane index (STN ISO 4264)	51.16	30 vol. %	242.5
Flash Point, °C	75	50 vol. %	266.3
Water content, mg/kg	36.7	70 vol. %	293.0
Ash content, wt. %	< 0.001	90 vol. %	329.4
Carbon residue, wt. %	< 0.01	95 vol. %	346.1
Total contamination, mg/kg	0.84	end of distillation	358.8
Copper strip corrosion (3 hr at 50 °C)	1a	Aromatic content, wt. %	31.50
Oxidation stability, g/m^3	0.0	— monoaromatics, wt. %	24.90
CLOUD point, °C	–8	— diaromatics, wt. %	5.90
Filterability, °C	–8	— triaromatics and higher, wt. %	0.7
Lubricity (wsd1.4), without additive	596	Polycyclic aromatic hydrocarbons, wt. %	6.6
Cetane number	49.9		



Scheme 1. Condensation reactions to synthesise MEAD and DEAD samples. R symbolised methyl, ethyl, and propyl group. Estimated yields are in parentheses (according to Pokorný and Dubská (1986)).

methods used are summarised in Tab. 2, where the technical standards and standardised procedures used are indicated (NACE TM0172-2015; Slovak Office of Standards, Metrology and Testing).

Quantum-chemical calculations

All calculations were performed using the Gaussian 16 program package (Frisch et al., 2016). The density functional theory with hybrid meta exchange-correlation functional M06-2X (Zhao and Truhlar, 2008) combined with the 6-311++G(d,p) basis set (Hariharan and Pople, 1973) was employed. The calculations performed at this theoretical level offer reliable description of thermodynamics of homolytic or heterolytic decay of N—H (Kováčová et al., 2023), O—H (Michalík et al., 2019), S—H (Rimarčík et al., 2011), C—CH (Lukeš and Hartmann, 2021), or C—CH_3 (Kleinová et al., 2024) bonds.

Optimisation of geometric structures was performed applying tight optimisation criteria and ultrafine DFT integration grid. True minima on the potential energy surface were confirmed through vibrational analysis (ensuring no imaginary frequencies are present). Thermodynamics of individual reactions were evaluated using reaction enthalpies for 298.15 K. Therefore, equilibria of studied reactions were not be discussed; reaction Gibbs free energy is beyond of the scope this publication (Atkins and Paula, 2006). Optimal geometries were visualised using the open-source Jmol viewer (Fig. 2) (Jmol

development team, 2016). Statical calculations were performed using exponential fit in OriginPro 2016 (OriginPro, 2016).

Results and Discussion

Theoretical calculations

Quantum-chemical calculations of the studied molecules were performed for gas-phase. Methyl- (Me), ethyl- (Et), and propyl- (Pr) groups (Scheme 1) were used as model alkyl chain (R) with expected induction effect along simple C—C bonds (Clayden, Greeves and Warren, 2012). Reactions A, B, C and F were mentioned according to (Pokorný and Dubská, 1986). Reactions D and E were suggested by authors for better understanding of the thermodynamics of investigated reaction schemes.

Since the studied molecules can have a larger number of conformations, only conformations with the occurrence of maximal number of intramolecular hydrogen bonds were considered. From a thermodynamic point of view, these conforma-

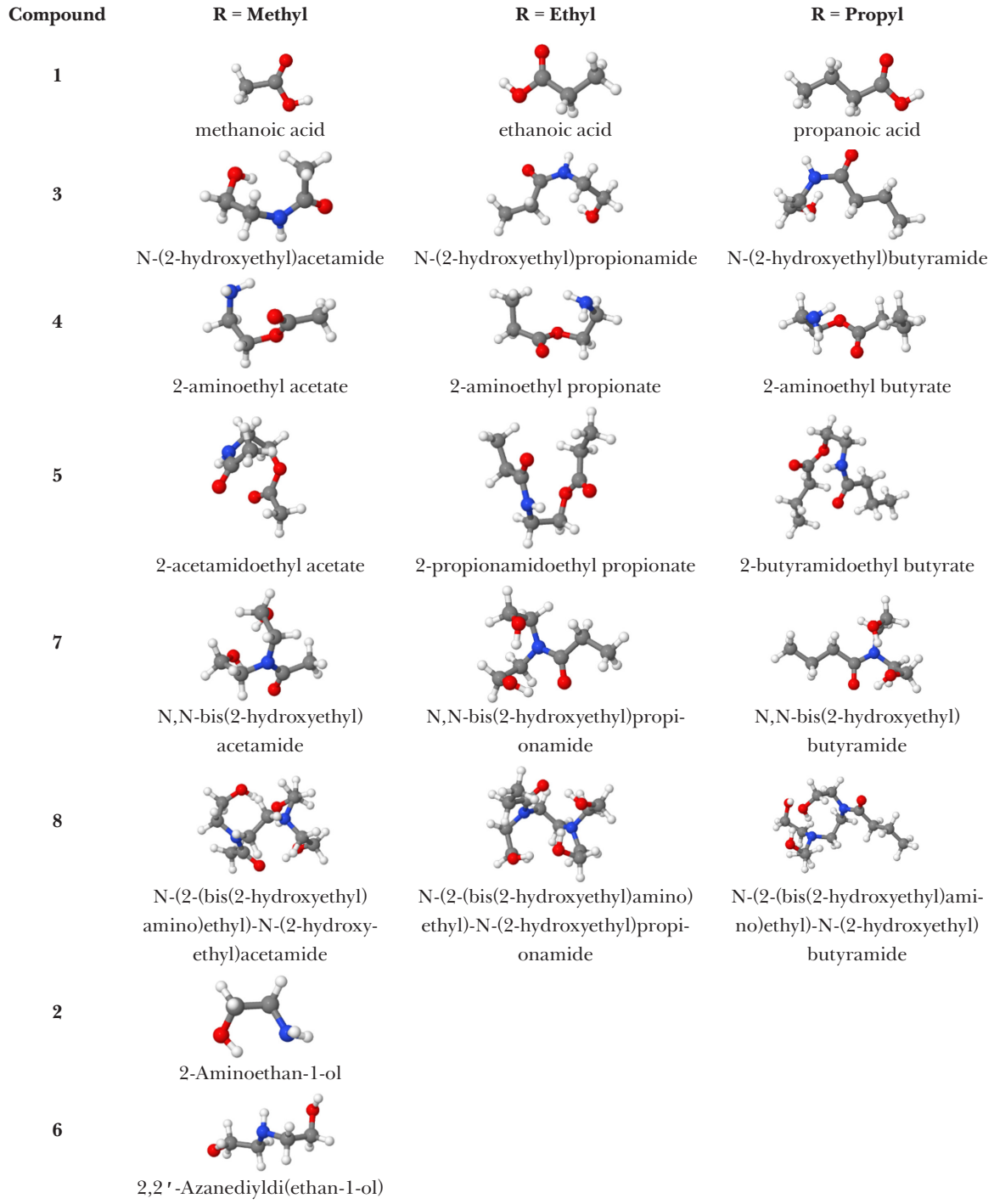


Fig. 1. Optimal geometries of studied molecules.

tions are the most energetically preferred and the most stable. This approach has been successfully used by Štellerová et al. (2022). Similarly to cyclic non-aromatic compounds, the presence of hydroxyl groups sterically modulates the geometry of organic molecule conformations (Rottmannová et al., 2013) and thus, *all*-trans conformer was considered for the propyl chain. Optimised geometries of studied organic molecules for individual substitutions of the alkyl group are shown in Fig. 1. Bond breakage in a molecule is caused by the formation of an intramolecular hydrogen bond between N—H and C—H. This phenomenon can be observed, for example, in case of MEAD, DEAD. It is typically the case if one intramolecular hydrogen bond exists within the molecules under study; however, in instances such as the product of reaction E (propyl group), multiple intramolecular hydrogen bonds are present.

Reaction enthalpies ($\Delta_r H$) were calculated as subtraction between calculated enthalpies of products and reactants with the corresponding reaction scheme (Scheme 1) in mind. As it is shown in Fig. 1, A and C reactions are considered as exothermic processes from the energetical point of view. Reaction enthalpies calculated for reaction A are –6 kJ · mol^{-1} for Me group and –4 kJ · mol^{-1} for Et and Pr groups. Similarly, substituent energies for Et and Pr groups for reaction C are comparable, i.e., prolongation of alkyl chain has only an insignificant effect on reaction thermodynamics. Reaction enthalpy for the largest model molecule with the Pr group was –19 kJ · mol^{-1} for reaction C. Reaction enthalpy of B reaction, 1 kJ · mol^{-1}, identifies weak endothermic process for the Et substituent group.

Exothermic character of chemical reactions is also predicted when reaction enthalpies for DEAD formation are considered. Higher reaction enthalpies were found for reactions A through C. It is worth to note that alkyl chain has more significant effect in E and F reactions. Elongation of the alkyl chain decreases the reaction enthalpy values by 2 kJ · mol^{-1} for hypothetical D reaction, 12 kJ · mol^{-1} for E reaction, and 13 kJ · mol^{-1} for F reaction compared to the Me group. The F reaction is the most preferred one for direct DEAD formation. Additional branching of the chain will possibly be energetically preferred as well. Energetical difference between E and F reactions is approximately 40 kJ · mol^{-1}.

Physicochemical measurements

The use of diesel fuel with very low sulphur content is associated with the need to adjust lubricity to avoid damage to selected aggregates and engine parts. Lubricity itself was expressed in this measurement as *WS1.4* in μm.

Lubricity of diesel fuel and MEAD and DEAD samples in diesel fuel was determined according to the High-Frequency Reciprocating Rig (HFRR) on a PCS Instruments HFR2 Specimens device according to STN EN ISO 12 156-1. The test principle is as follows: the fuel sample to be tested is placed in a small test vessel tempered at 60 °C. A fixed steel ball is clamped in a vertically mounted fixture and is pressed against a horizontally mounted static plate (plate) by means of an applied load. The test ball oscillates at a constant frequency at a constant stroke and the contact surface of the ball and the plate is completely immersed in a small vessel of the test device filled with the test sample. Metallurgical quality of the plate and ball as well as the test con-

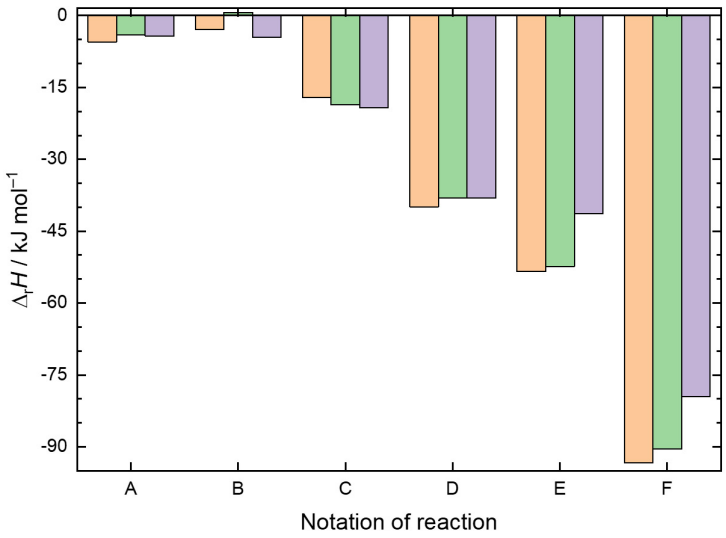


Fig. 2. Comparison of reaction enthalpies for studied types of reactions in dependence on alkyl chain length. Notation: methyl- (orange), ethyl- (green) and propyl- group (purple).

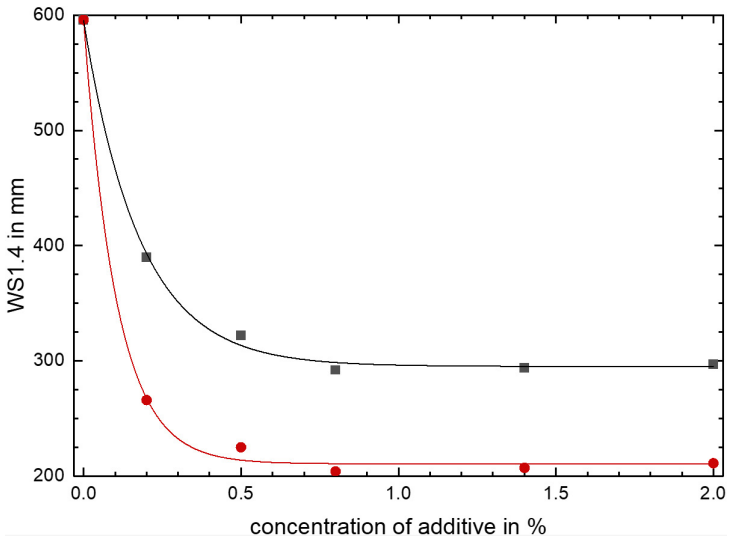


Fig. 3. Dependence of lubricity on the percentage concentration (c) of additive MEAD and DEAD.

ditions (fuel temperature, ball weight, frequency, stroke size, and test time) are specified in the standard. Diameter of the abrasion mark (MWSD value) after the test is read using a microscope and it is corrected depending on the temperature and humidity at the beginning and end of the test. The corrected diameter (WS value of 1.4) is a measure of the lubricity of the tested sample and the estimated uncertainty for this experiment is 2 %.

The tests showed that the synthesised MEAD and DEAD affect the lubricity; the dependences of lubricity on concentration (*c*) are shown in Fig. 3.

The obtained dependences satisfy the form of an exponential function with parameters of the linearised function:

$$WS1.4/\mu m = y_0 + A \times \exp(B \times c) \quad (1)$$

where c denotes the percentage concentration of the additive. Regression parameters y_0, A, B, and coefficient of determination (R^2) obtained from regressions are summarised in Tab. 3. Therefore, if R^2 is above 0.9980, the function correctly describes the concentration dependence of lubricity.

Tab. 3. Regression parameter of Eq. 1 and coefficient of determination for MEAD and DEAD.

	MEAD	**DEAD**
y_0	295.2 ±3.8	210.6 ±4.1
A	300.3 ±7.5	385.3 ±8.9
B	–5.60 ±0.38	–9.56 ±0.78
R^2	0.9981	0.9984

Comparison of the curves shows that the measured value of WS1.4 decreased significantly below the limit required by the Slovak Technical Standard STN EN 590, this condition was met already at the lowest investigated additive concentration. DEAD alone has a 10 % higher efficiency than MEAD. The estimated limit value is 210.6 μm.

Cetane number (CN) of diesel fuel and MEAD and DEAD samples in diesel fuel were determined according to STN EN ISO 5165 on a Waukesha test engine (STN EN ISO 5165). Results of the measurements are presented in Tab. 4, showing no positive effect of amides on the CN increase and the CN

Tab. 4. Effect of MEAD and DEAD addition (in wt. %) on the antifoaming properties of diesel fuel and on the cetane number of diesel fuel.

Percentage	0.0	0.2	0.5	0.8	2.0
MEAD					
cetane number	49.9	49.5	48.7	48.4	48.8
Foam break-up time/s	28.5	2.87	4.4	4.3	9.5
Foam height/mL	86	16	25	30	35
DEAD					
cetane number	49.9	49.9	49.9	49.5	48.3
Foam break-up time/s	28.5	43	19	22	31
Foam height/mL	86	86	75	77	83

even decreases with the increasing concentration. This fact was verified at a concentration of 20 wt. % of MEAD when the cetane number decreased to 47.3. Therefore, the estimated uncertainty for measured cetane number is ±0.2, the presented experiment indicates minimal effect of the studied additives on CN.

Antifoaming properties of the synthesised MEAD and DEAD additive samples were evaluated according to the French standard AFNOR NF M 07-075 (*Détermination de la tendance au moussage de gazoles*). In this test, a quantity of diesel fuel is injected at constant pressure into a calibrated glass measuring cup. The volume of foam produced, and the time taken for the foam to break up are then measured. Results of the effect of MEAD and DEAD addition on the antifoaming properties are summarised in Tab. 4. The MEAD sample was found to have very good antifoaming properties. The DEAD sample failed in this test because it had high foaming characteristics. The values for DEAD ranged from 75 to 86, with similar values achieved for 0.2 % and 2.0 %. MEAD addition showed better antifoaming properties compared to DEAD. The estimated uncertainty for measured antifoaming properties is 3 %.

Conclusions

This work was devoted to theoretical and experimental study of MEAD and DEAD samples. Thermodynamics of the relevant reactions leading to the production of the studied substances and by-products indicate exothermic nature of the reactions. The influence of the increase in the alkyl chain was demonstrated in case of DEAD formation. The syntheses of MEAD and DEAD were done employing the internal synthetical treatment. The final product can be separated on a molecular evaporator by distillation. Preliminary experimental characteristics of diesel fuel with MEAD or DEAD addition showed only a negligible positive effect on the cetane number. Lubricity properties of the samples were observed even at low MEAD and DEAD concentrations. While the MEAD sample showed good antifoaming properties, the DEAD sample did not have a significant effect on the antifoam properties.

It can be concluded that the addition of MEAD (0.2 wt. %) to diesel fuel is perspective for the preparation of novel types of fuels. Nevertheless, complex experimental characterisation of prepared samples should be presented in a systematic form.

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