Wrocław University of Technology
Faculty of Geoengineering, Mining and Geology

APPLICATION OF MICROEMULSION FOR UPGRADING DIFFICULT-TO-FLOAT MATERIALS

by
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Thesis submitted to
Wrocław University of Technology
Faculty of Geoengineering, Mining and Geology
in partial fulfillment of the Ph.D. degree

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Wrocław, 2005

Politechnika Wrocławska
Wydział Geoinżynierii, Górnictwa i Geologii

ZASTOSOWANIE MIKROEMULSJI DO WZBOGACANIA MATERIAŁÓW TRUDNO FLOTUJĄCYCH

(APPLICATION OF MICROEMULSION FOR UPGRADING DIFFICULT-TO-FLOAT MATERIALS)

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Wrocław, 2005

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ACKNOWLEDGMENTS

I would like to express my deepest thanks, gratitude and appreciation to Prof. Dr. Eng. Jan Drzymała, my supervisor, first for his kind hospitality during my stay in Poland, second for his valuable guidance, discussion and support throughout the course of this investigation. Thanks are also extended to Prof. Dr. Eng. Andrzej Łuszczkiewicz, head of Mineral Processing Laboratory during the carry out of this work, for his advices. I would like also to thank all members of the Mineral Processing Laboratory, Department of Geoengineering Mining and Geology, Wrocław University of Technology, for their keen help which made everything available and possible. Their help and friendship will be always remembered.

I could not forget to express my appreciation to my parents and my smaller family for their patience on my being abroad. Their love, support, and encouragement helped me a lot to carry out this work.

Hussin A. M. Ahmed
Wrocałw, Poland, 2005

1. Introduction

1.1. Structure of the thesis

The thesis is divided into four parts. The theoretical background (part 1) deals with the literature review on upgrading difficult-to-float materials and flotation reagents such as collectors, frothers, modifiers, and mixed collectors. The physico-chemical properties of flotation reagents forming microemulsions, emulsions and surfactant solutions were discussed. In addition, a detailed background on microemulsion as a special form of mixed collectors, containing definitions of microemulsions, their creation, types, properties and applications was presented (part 1, section 2). The ways of evaluation of flotation results were also reviewed in the theoretical part. First, graphical representation of experimental results containing from one to many variables and a response were considered (part 1, section 3). Next, judgment, evaluation, and/or comparison of separation data applying various upgrading curves was discussed. A list of mathematical equations was proposed for delineation of upgrading results using the so-called Fuerstenau upgrading curves (part 1, section 4).

The investigatory part (part 2) describes materials and procedures applied to carry out the experimental work (part 2, section 5). It also presents the results obtained and their discussions (part 2, section 6). The results include flotation of an oxidized coal as a difficult-to-float material in the presence of different collectors, frothers and their combinations applying the well-known flotation procedure. An evaluation of flotation results suggested investigation of the considered flotation reagents using another approach called here the direct-contact flotation procedure that is in the presence of anhydrous pure flotation reagents. Finally, additional flotation tests were carried using different structures of water-reagents mixtures, especially microemulsions, with oxidized coal to establish the most suitable procedure for its processing. An influence of moisture content on oxidized coal flotation was also investigated.

The concluding part of the thesis (part 3) contains general discussion of the obtained results followed by summary and conclusion drawn from the work.

Finally, the last part (part 4) lists the sources of the literature data used in the work.

1.2. Background and aim of the thesis

Flotation is one of the most widely used processes in mineral processing. The technique holds its importance because of the ability to process fine-size fractions of low-grade ores. Research on flotation showed that there are some easily floatable materials because of their natural hydrophobicity, while others show some difficulties during their processing. To achieve successful flotation of such difficult-to-float materials, numerous ideas have been examined. These proposals were devoted mainly to ores, flotation machines, air-bubbles and applied reagents. Within the first trend, attention was paid to preparation steps of the ore. It included, in addition to liberation considerations, size, roughness and shape of particles fed to flotation and the percentage of fine materials included in the feed. Regarding flotation equipment, some researchers tried variation of equipment design in addition to optimizing the number of cells used simultaneously for scavenging, roughing, and cleaning steps. Others investigated operating parameters affecting the performance of flotation machines. A development of the flotation column represents a result of equipment research in the flotation area. Another research trend was devoted to flotation reagents. The goal of such investigations was to select appropriate collector-frother pairs for a given flotation system. Numerous studies dealt with collector-frother interactions and their role in flotation of difficult-to-float materials. Others recommended the use of reagent or mixture of reagents with special chemical structures to serve as collectors. For example, hydrocarbon poly(ethylene glycol) ethers were successfully applied for flotation of difficult-to-float oxidized coal. A literature survey showed that application of mixed ionic-nonionic or mixed anionic-cationic surfactants in the form mixtures of collectors were found to be successful.

This thesis is a continuation of research related to the role of special reagents and flotation procedure in processing of difficult-to-upgrade materials. It includes a number of flotation reagents that will be used individually or in different combinations for flotation of oxidized coal as an example of carbon bearing difficult-to-float materials. The thesis concentrates on the application of microemulsion formed by flotation reagents in water for flotation of difficult-to-float oxidized coal. For comparison purpose, anhydrous reagents and other structures of flotation reagents in water as surfactant solutions, liquid crystals, and emulsions were considered. The main aim of this thesis is to show the influence of the microemulsion formed from flotation reagents on the flotation results of difficult-to-float materials.

1.3. Contribution of the thesis

There are several contributions resulted from this thesis. The first one involves a methodology for a systematic graphical presentation of complex separation elements containing from one to many variables (up to three) and a response. Having this methodology, it becomes easy to choose the right and most suitable plot for representing the obtained data (part 1, section 3).

One of the tasks of this thesis was to compare separation results obtained from different flotation series. It is well known that the results of most separations can be presented graphically as a two-parameter relationship representing quantity and quality of products of separation. One of many separation plots is the Fuerstenau upgrading curve, which relates recoveries of components in the different products of separation for example recovery of carbonaceous matter in concentrate versus ash recovery in tailing. It became necessary to create a list of mathematical formulas for approximation of the data plotted as the Fuerstenau curve. It was shown in the thesis that a given set of upgrading data can be approximated with a reasonable accuracy using different mathematical formulas as well that different sets of data can be approximated with the same formula. It was also shown that a one-parameter equation can provide a selectivity index that can be used for comparing results of different separation series of data (part 1, section 4).

A next contribution of the thesis was development and application of a unique flotation procedure to determine the best possible separation results. The procedure is based on mixing dry coal with flotation reagents. It was called, in this thesis, the direct-contact flotation procedure or shortly DCF. The DCF procedure is especially applicable to flotation of difficult-to-float oxidized coal. It shows the potential (maximum possible recovery and selectivity) of cleaning of difficult-to-float oxidized coals by flotation.

One more contribution is the finding that microemulsion formed with flotation reagents in water is very powerful in processing difficult-to-upgrade coals. Its drawback, however, is a high dosage of reagents which has to be used for successful separation. It was also found that the same effect can be accomplished by a direct mixing of anhydrous reagents with coal having a given moisture content. The anhydrous reagent together with the moisture coming from coal spontaneously form microemulsion which improves the results of flotation.

THEORETICAL BACKGROUND

2. Flotation

2.1. Flotation principles

Flotation is a unit operation separation technique. A flotation system consists mainly of three phases, that is solid particles, air bubbles, and aqueous phase. Flotation takes place when particles of one or more minerals adhere preferentially to air bubbles passing upwards through the pulp (Fig. 1). To achieve flotation of a certain type of particles from the pulp, usually their surface must be made more hydrophobic using appropriate reagent or reagents (Gaudin, 1939).

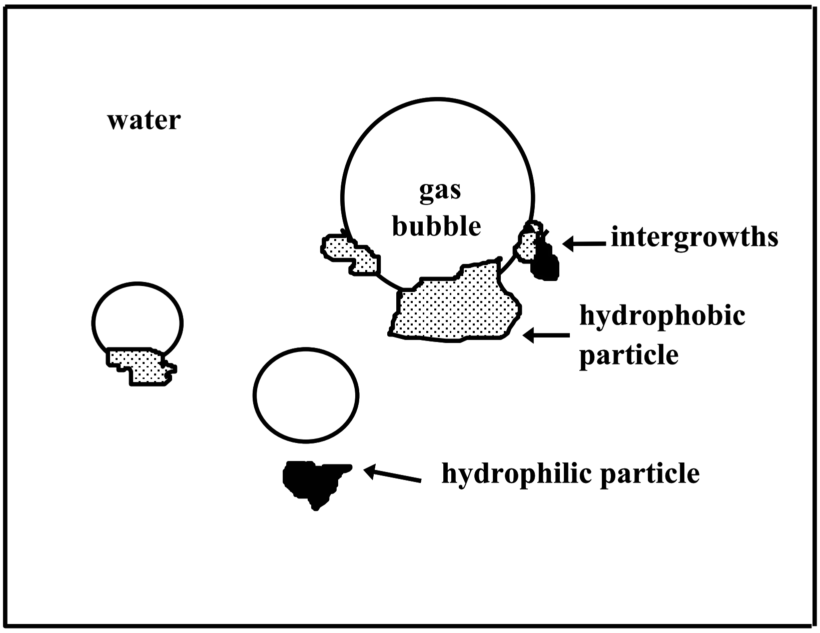


Fig. 1. Fixation of particles with hydrophobic surfaces to air bubbles leading to flotation (after Drzymala, 2001a)

The first preparation step of flotation is dispersion of particles using stirring and, if necessary, adding reagents to disperse particles, especially when they are fine and tend to aggregate with hydrophilic particles. It is beneficial when the dispersion is followed by particles attrition to clean their surface and partially liberate them from surface oxidation products (Wills, 1992). For the attrition to be effective, the impeller-rotational speed and pulp density must be relatively high (Gutierrez, 1977). When the particles to be concentrated are highly naturally hydrophobic, simple aeration after the two previous steps can lead to flotational separation.

Reagents, which make the surface of particles hydrophobic, are referred to as collectors. They may be classified according to different bases (Table 1).

Table 1. Different classifications of flotation collectors (based on various sources)

Base	Classes	Types	Examples	Reference
Ionicity	Nonionic	Oils	Hydrocarbons and their derivatives	Gaudin, 1939; Fuerstenau, 1995
		Surfactants	Hydrocarbon poly(oxyethelene glycol) ethers Ethoxylated sorbitan fatty esters Sulfoxides	
	Ionic	Anionic	Carboxylates, $R(COO)^-$ Sulfonates, $R(SO_3)^-$ Alkyl sulfates, $R(SO_4)^-$ Hydroximates, $RNH(COO)^-$	
		Cationic	Primary amines, $R(NH_3)^+$ Secondary amines, $RR'(NH_2)^+$ Tertiary amines, $R(R')_2NH^+$ Quaternary ammonium salts, $R(R')_3N^+$	
Bonding	Adhesion	Oils	Hydrocarbons and their derivatives	Fuerstenau et al., 2000; Drzymala, 2001a
	Hydrogen bonding	Nonionic surfactants	Hydrocarbon poly(oxyethelene glycol) ethers Ethoxylated sorbitan fatty esters Sulfoxides	
	Chelating	N-N	Diamines	
		S-O	Monothiocarbonates	
		S-S	Xanthates	
		N-S	Carbomates	
		O-O	Fatty acids	
		N-O	Oximes	

R and R' represent hydrocarbon radicals

Within the first classification, the collector can be either apolar (nonionic surfactant or oil) or polar (anionic or cationic surfactant). Oils have low solubility in water and in most cases are used for flotation of minerals having natural hydrophobicity. On the other hand, the polar collector molecule consists of polar and non polar parts. The polar section is adsorbed at the surface of the particle while the non polar section is oriented to the outside aqueous phase (Gaudin, 1939)(Fig. 2). Polar collectors are further classified according to the type of ion formed upon their dissociation in aqueous solutions as anionic or cationic. Anionic collectors, for instance, include Carboxylates, Hydroximates, and alkyl sulfuric salts. Cationic collectors, less widely used, contain amine groups. Amine type collectors are water insoluble and require the presence of acids to induce solubility (Wills, 1992).

Within the second classification, flotation collectors are divided according to the mechanism by which they are bonded to the particle surface. The oils are usually linked with particles by adhesion, nonionic surfactants by hydrogen bonds, while the chelating reagents by chemical reaction (Drzymala, 2001a).

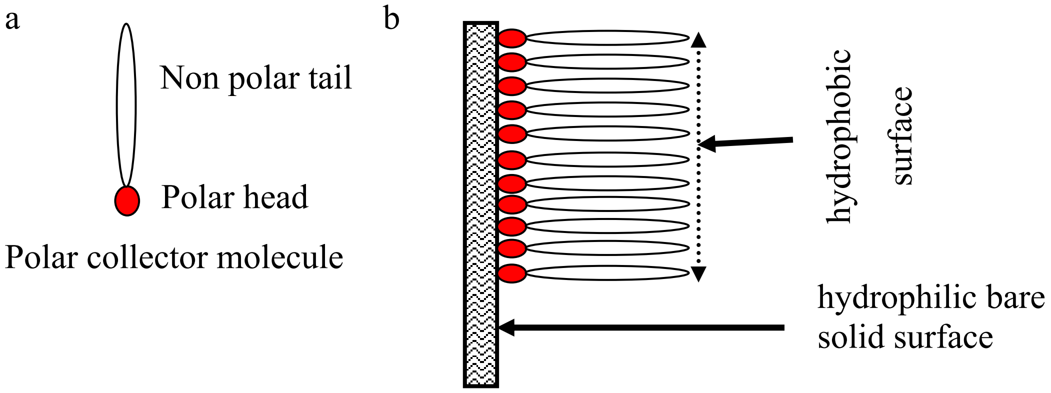


Fig. 2. Collector changes hydrophilic mineral surface to hydrophobic. a) structure of polar collector molecule, b) adsorption of polar collector at polar surface sites. Chemical bonding between mineral surface and collector molecule can be electrostatic, covalent, or electrostatic-covalent in nature

For successful flotation, additional reagents such as frothers and modifiers are used. Frothers are organic surfactants that should preferentially be absorbed at the air/water interfaces. The functions of frother in flotation are:

- reducing the surface tension of the air–liquid interface, resulting in a stable air-bubble in the system (Leja and Schulman, 1954)
- improving the kinetics of bubble–particle adhesion (Leja, 1956)
- thinning the liquid layer between the solid particle-air bubble interfaces by interacting with collector molecules (Leja, 1956; 1982)
- stabilizing the bubble–particle aggregates (El-Shall et al., 2000)
- preventing coalescence of bubbles (Laskowski, 2004).

Frothers used in flotation were classified into surface-active and surface-inactive types (Lekki and Laskowski, 1975; El-Shall et al., 2000). Other classifications, based on the frother chemical composition and properties such as hydrophobic-lipophilic balance (HLB), dynamic foamability or frothability index

(DFI) combined with bubble critical coalescence concentration (CCC), are also available (Laskowski, 1998; 2004) (Table 2). The last classification seems to be the most practical. It characterizes frothers with two parameters that are DFI and CCC. The frothers with large CCC and small DFI are called selective, while those with small CCC and large DFI are described as powerful (Laskowski, 2004).

Table 2. Different classifications of flotation frothers (after different sources)

Base	Classes	Examples	Remarks	Reference
Surface activity	Surface active frothers	Fatty acids and amines	Colloidal solutions decrease surface tension	Lekki and Laskowski, 1975; El-Shall et al., 2000
	Surface in-active frothers	Alcohols	Molecular solutions decrease surface tensions	
		Diacetone and ethyl acetal alcohols	Molecular solutions do not change surface tension	
		Inorganic electrolytes	Molecular solutions raise the surface tension	
Chemical composition	Aliphatic alcohols ROH	MIBC (methyl isobutyl carbinol) 2-ethyl hexanol Diacetone alcohol TEXANOL (2,2,4-trimethylpentanediol 1.3-monoisobutyrate)	Low solubility in water Low solubility Very good solubility Insoluble in water	Laskowski, 1998
	Cyclic alcohols	α-terpineol (effective reagent of pine oil) Cyclohexanol	Low solubility in H_2O Low solubility in H_2O	
	Aromatic alcohols (Phenols)	Mixture of cresol and xylenol (cresylic acid)	Low solubility in water	
	Alkoxyparaffins	TEB (1,1,3-triethoxybutane)	Low solubility in water	
	Polyglycols	Poly(propylene glycol) monoalkyl ethers ($R(OC_3H_6)_nOH$), as DF-250 ($CH_3(PO)_4OH$) DF-1012 ($CH_3(PO)_{6.3}OH$) DF-400 (Aerofroth 65) ($H(PO)_{6.5}OH$)	Good solubility in water Totally soluble 32 % solubility Totally soluble	
		Poly(ethylene glycol) $R(OC_2H_4)_nOC_2H_4OH$	Good solubility in water	
	Other	Sulfo-cetyl alcohol $CH_3(CH_2)_{14}CH_2OSO_2OH$		
Chemical properties	HLB	F-937 (Allied Colloids Precol) F-114 (from Witco Arosurf) F-140 (from Witco Arosurf)	frothers are MIBC like commercial products with different HLBs	Laskowski, 1998
		Most good frothers have HLB values close to 6,	They cooperate actively with the adsorbed collector	Polat et al., 2003
	DFI and CCC	Each frother is characterized with DFI and CCC values	They define frother as powerful or selective	Laskowski, 2004

Modifier is a broad name for depressants, activators, pH regulators, and other reagents. Depressants are species that selectively cover the surfaces to make them hydrophilic. The use of depressants increases the selectivity by preventing flotation of undesirable particles (Wills, 1992). Activators are generally soluble salts that ionize in water. The ions in solution react with the surfaces to favor the adsorption of a collector. They act oppositely to depressants. pH controllers are compounds usually used to adjust pulp pH required for optimal particle, collector, frother, depressant and activator behaviour (Wills, 1992).

According to Wills (1992), usually flotation efficiency increases when each reagent is added one at a time. The order in which the reagents should be added is presented in Fig. 3. This order is established by the nature and function of the reagent. When adding a collector, depressant or activator, the conditioning time must be sufficient to allow various phenomena to occur (Wills, 1992). Since each ore is unique, the flotation reagents and the adequate conditions must be studied in laboratory by testing each situation.

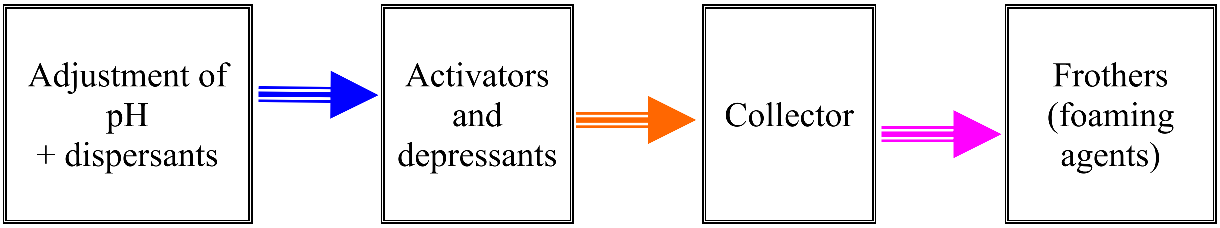


Fig. 3. Usual sequence of flotation reagents addition during pulp preparation based on their function (after Wills, 1992)

For flotation, mechanical, pneumatic, and mechanical-pneumatic machines are used. Flotation column is a pneumatic device especially efficient in processing fine particles (Amelunxen, 1985; Luttrell et al., 1991; Ayhan, 2002). It has two main advantages over the other flotation machines. First, entrainment is reduced by the addition of wash water. Second, the chances of collision between air bubbles and particles are high due to the height of the column, which can be up to ~14 meters for industrial applications (Kelly and Spottiswood, 1982).

Flotation circuits may contain several flotation machines in series or in parallel. The terms scavenging, roughing, and cleaning are used to describe the various functions of the flotation step (Kapur and Mehrotra, 1974; Agar et al., 1980; Sutherland, 1981; Green, 1984).

The effectiveness of flotation depends on the nature of the raw material (Bujnowska, 1985; Arnold and Aplan, 1986(a-c); 1989; Ayat, 1987; Kars-ilayan et al., 1992). The first and most important factor related to floating material is its particle size (Tsai, 1988; Vanangamudi et al., 1989). Many studies have been conducted to determine the effect of particle size, shape and degree of particle locking (liberation) on coal flotation. For example, Vanangamudi and Rao (1989) concluded that the flotation rate depends strongly on particle size but not as much on particle shape. The particle size corresponding to maximum flotation rate and recovery was found to vary widely depending on the operating conditions (Robinson, 1960; Rastogi and Aplan, 1985; Polat et al., 1993, 1994a). Flotation can be used to process particles with a diameter approximately between 5 and 200 µm. However, for light minerals such as coal, the upper limit can be up to 1.7 mm (Polat et al., 1993). The upper size limit of flotation is determined by the capacity of the air-bubbles assemble to lift a given weight (Wojcik et al., 1989; 1990; John et al., 1999). It is sometimes important to remove coarse particles from the pulp before flotation. On the other hand, the presence of ultra-fine particles has a negative effect on flotation (Flynn and Woodburn, 1987a,b). Their presence increase collector consumption and hamper selectivity due to unavoidable entrainment effects.

Flotation can be treated as an outcome of different sub-process taking place among three phases interacting in water, that is particles, reagents droplets, and air bubbles. Sub-process includes collisions between the same or different components of the flotation system. Figure 4 shows a schematic representation of the particle-collector droplet-air bubble system representing coal floated with apolar oils (Polat et al., 2003). For the air-particle-oily collector system, the collisions may lead to coalescence or aggregation of one component (air bubbles together or reagents droplets) or attachment/detachment of two different phases (air bubble/reagent droplet, reagent droplet/solid particle, solid particle/air bubble). Flotation needs preferential attachment of reagent droplets with solid particles and then with air bubbles.

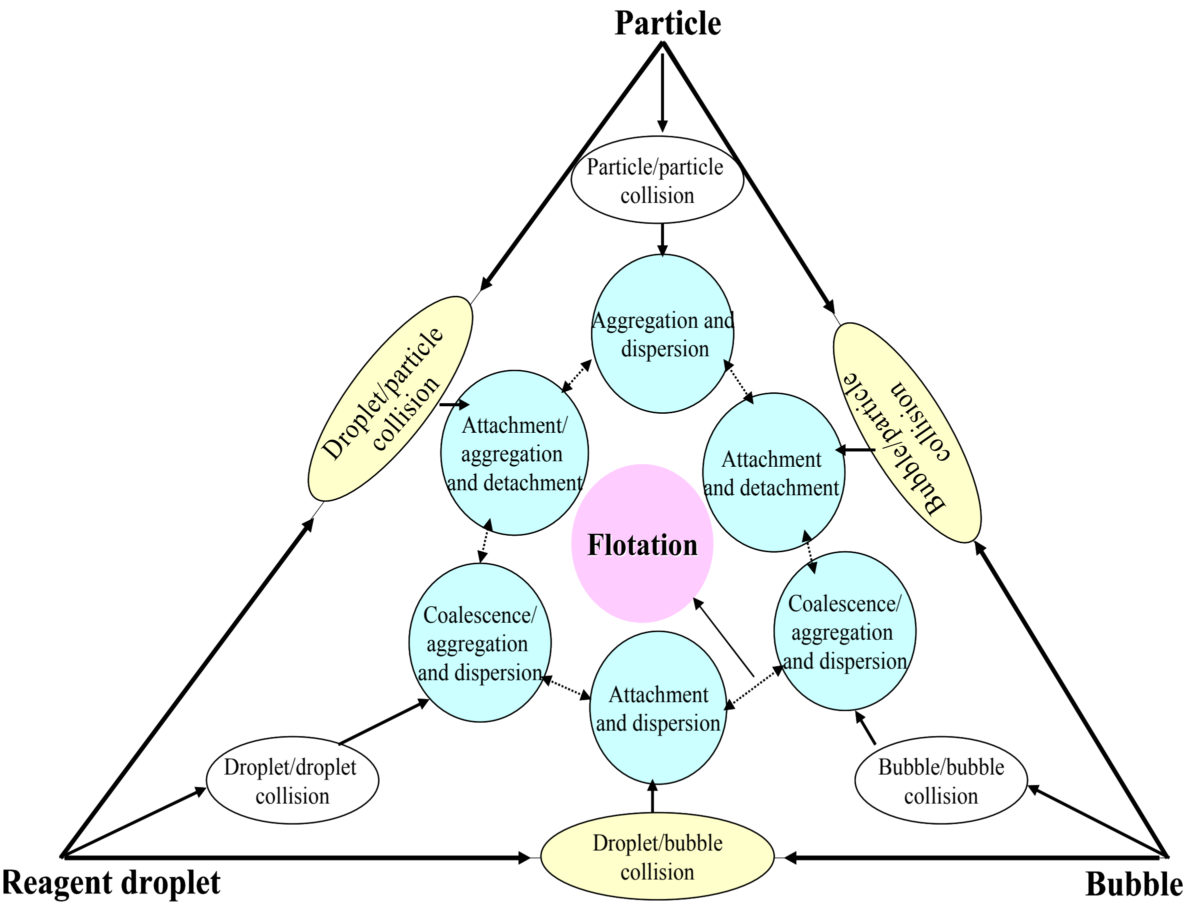


Fig. 4. Schematic representation of various sub-processes that may occur during coal flotation using oily collectors (this author scheme, based on data of Polat et al., 2003)

Polat et al. (2003) categorized flotation factors into four categories. They are: material, chemical, operational and equipment parameters. They differentiated three levels parameters contained in a certain category. For instance, the parameters that might fluctuate and need adjustment on a regular basis (e.g. daily) were referred to as Level I. Those that are set during the design stage or after a major renovation were referred to as Level II, while parameters not controlled, due to inherent material characteristics and practical limitations, were nominated as Level III. Table 3 shows a list of the parameters contained in each category at the different levels.

Table. 3. Parameters affecting the flotation process (after Polat et al., 2003)

Parameter → Level ↓	Material parameters	Chemical parameters	Equipment parameters	Operational parameters
Level I	Particle size Liberation Composition	Reagent concentration (collector, modifier and frother)	None	Conditioning Aeration and froth parameters Mode of chemicals addition
Level II	Particle size Liberation	Reagent type (collector, modifier and frother)	Type of equipment and its design, circuit configuration	Impeller speed Density Pulp level Feed rate Conditioning Procedure
Level III	Mineralogy Composition Oxidation	Mineral/s (chemistry and their solution)	Best available technology	Temperature

2.2. Flotation reagents

2.2.1. Surfactant solutions

2.2.1.1. Properties

Majority of flotation collectors are surfactants. Surfactants are amphiphilic molecules containing hydrophobic segment, called “the tail” and hydrophilic segment called “the head” (Fig. 2; Fig. 5a). When a surfactant is dissolved in water at low concentrations, the molecules exist as individual entities called monomers (Israelachvili et al., 1976) (Fig. 5b). However, as the concentration of the surfactant increases, the molecules tend to associate, and the hydrophobic tails aggregate together, leaving the head groups (hydrophilic segments) exposed to the aqueous phase (Hua and Rosen, 1988; Sawyer et al., 1994) (Fig. 5c).

The simplest structures of surfactant aggregates are pre-micelles (Fig. 5c). A further increase in the surfactant concentration leads to the formation of micelles (Fig. 5d). The transition from a monomeric surfactant form in the aqueous phase to pre-micellar (pre-CMC) and micellar structures usually occurs at a certain concentration called the critical micelle concentration or CMC (Mukerjee and Mysels, 1971). It can be seen as a change in the slope of plots of many physical properties (e.g., surface tension, viscosity, conductance etc.) against surfactant concentration (Armstrong, 1985; Patist et al., 2000). Depending on the chemical properties of the surfactant, its concentration in the continuous phase and temperature of the system, the aggregation of micelles lead to the formation of more complex micellar forms (large micelles) (Lang and Eyring, 1972; Lang et al., 1972; Strey and Pakush, 1986; Mortensen, 2001) (Fig. 5e).

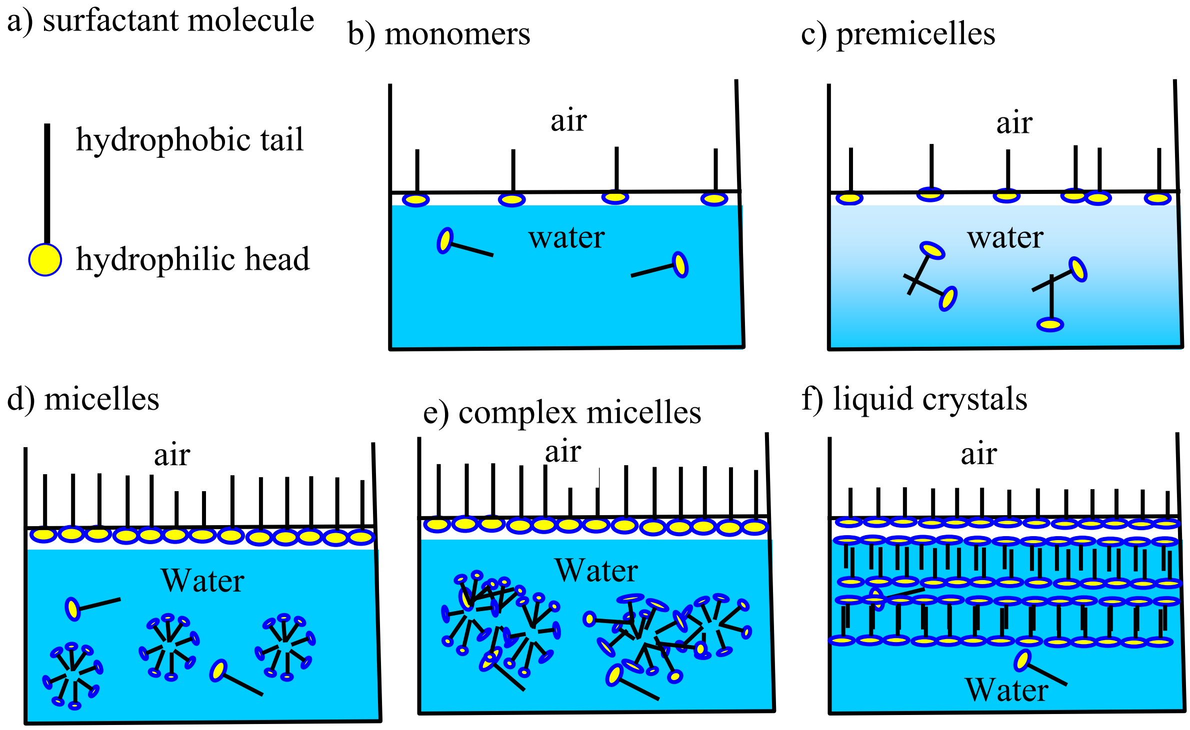
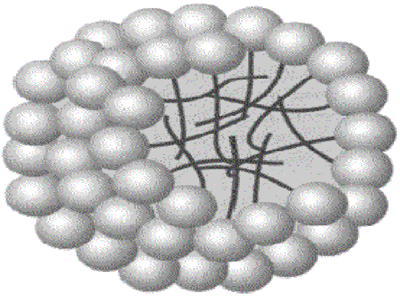


Fig. 5. Surfactants in aqueous solutions, a) surfactant molecule, b) at low concentration surfactant molecules are single, c) at higher concentrations surfactant begins to associate forming loose aggregates called pre-micellar structures and accumulate at interfaces leading to noticeable decrease in surface tension, d) micellar structure of surfactant in water begins to form at CMC, e) at higher concentration complex micellar forms occur, f) at still higher concentrations complex micellar structures change into liquid crystals followed by precipitation (after different sources see text)

Figure 6 shows in more details the complex normal micellar structures at fairly higher concentrations than CMC. They are mainly spherical and cylindrical in shape. At still higher concentration of surfactants in the solutions different forms of liquid crystals are formed (Winsor, 1972) (Fig. 5f). They include hexagonal, bicontinuous, and lamellar liquid crystals. Hexagonal liquid crystals are the first stage after complex micellar forms. They are arranged as close-packed cylinders forming cubic structures shortly named *H* (Fig. 7a). A further surfactant concentration increase in water gives a lamellar phase (abbreviated in literature as L, D, L_α or L_a) (Fig. 7b). A bicontinuous cubic phase, which is intermediate between the hexagonal and the lamellar phases, is a three-dimensional periodic arrangement where both water and surfactant form continuous networks (Fig. 7c). Thus, with increasing surfactant concentration, the hexagonal (*H*), bicontinuous cubic (*Q*), and lamellar (L, D, L_α or L_a) structures can be formed in that mentioned sequence (Friberg, 1999; Mortensen, 2001; Stephen, 2001).

a) spherical normal micelle



b) cylindrical normal micelle

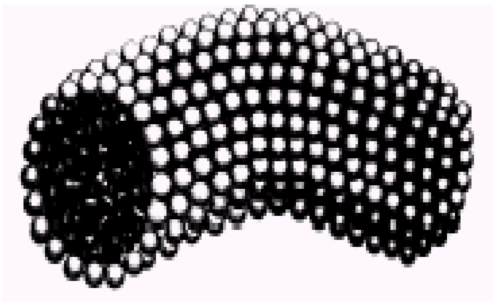
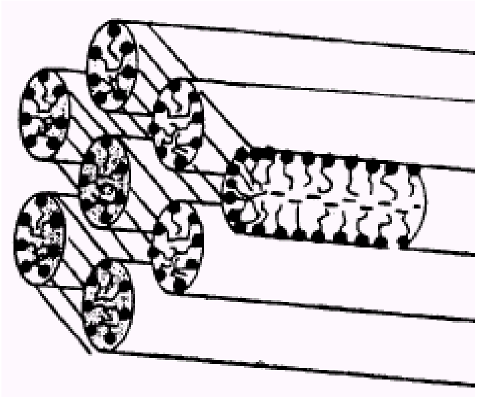


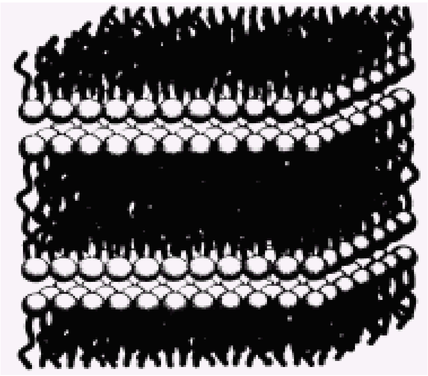
Fig. 6. Complex micelle structures into which surfactants aggregate in solution at concentrations above CMC, a) spherical normal micelle, b) cylindrical normal micelle, both of them have the polar head towards the aqueous phase while the non polar tail oriented interiorly, the formation of any of them depends on physico-chemical properties of surfactant in water (Inoue et al., 1980; Mortensen, 2001)

The simple and complex structures hitherto discussed are valid for both nonionic and ionic surfactants in water. However, their properties, and thus phase diagrams can be slightly different as it is shown in Fig. 8. The difference is that nonionic surfactants precipitate above certain temperature called the cloud point temperature (or CPT) (Fig. 8a) (Vincenzo et al., 2002), while the precipitation of ionic surfactants occurs below a certain temperature called the Kraft point temperature (or KPT) (Fig. 8b) (Gu and Sjöblom, 1992).

a) Hexagonal liquid crystals **(**H**)**



b) Lamellar liquid crystal (L, D, L_α, or L_a)



c) Bicontinuous liquid crystal structure (Q)

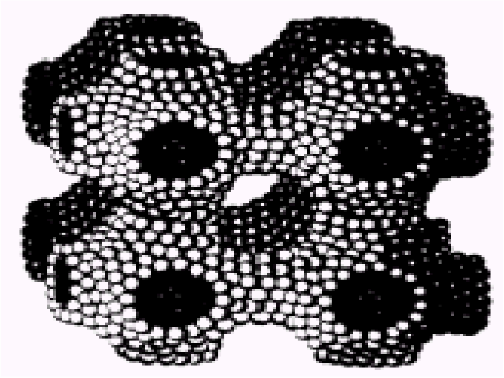
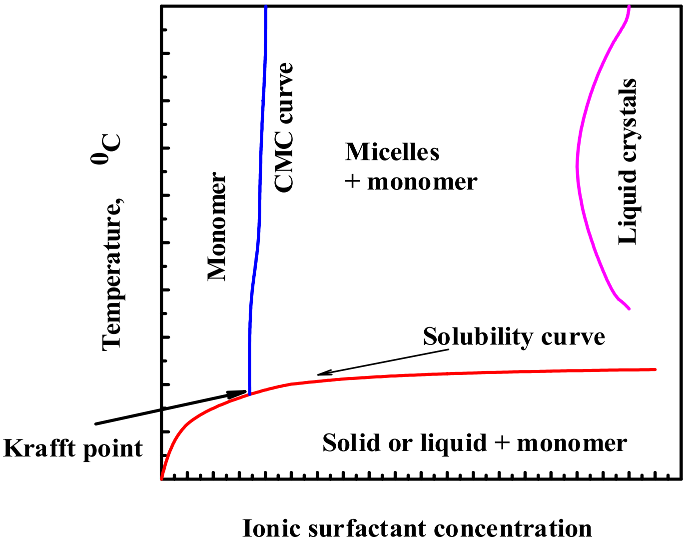


Fig. 7. Liquid crystal structures formed by surfactants in water. Figs. a-b represent ordered liquid crystal structures such as hexagonal and lamellar, respectively, while Fig. c shows disordered bicontinuous liquid crystal structure (Stephen, 2001)

a



b

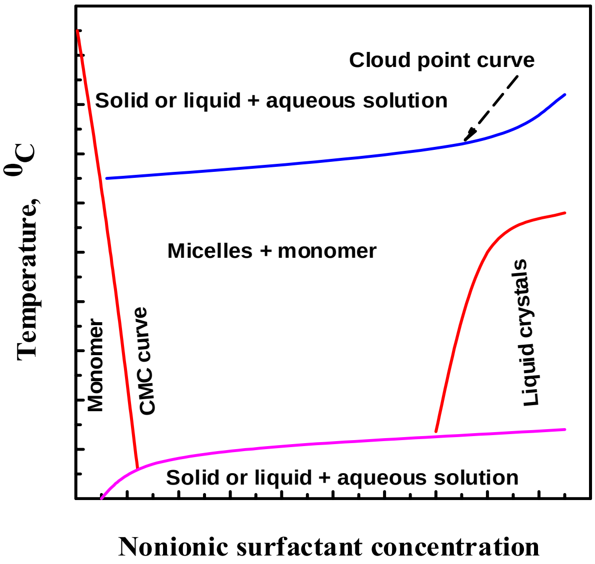
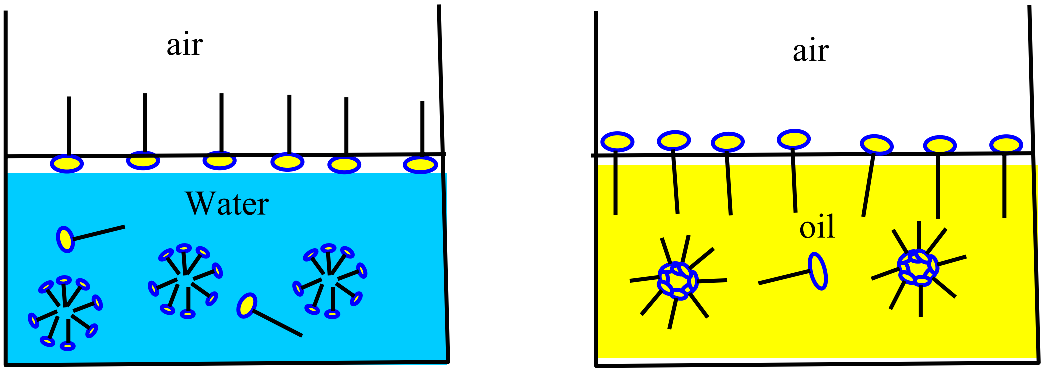


Fig. 8. Phase diagrams of surfactants as a function of temperature, a) ionic surfactants (after Armstrong, 1985), b) nonionic surfactants (after Gu and Sjöblom, 1992; Vincenzo et al., 2002)

At surfactant volume fractions in water that are significantly higher than 0.5, the inverse analogs of the structures shown in Figs. 5-7 are expected to be stable. These are the inverse or inverted micelles (L_2) (Fig. 9), the inverse cylindrical or spherical micelles, inverse bicontinuous cubic (*IQ*), the inverse hexagonal (*IH*) and the inverse lamellar structure (IL_α). In such inversed analogs, the surfactant acts as a solvent, where its head groups (hydrophilic segments) associate together keeping water inside them, leaving the hydrophobic tails exposed to the dominant surfactant phase (Linhananta and Sullivan, 1998; Stephen, 2001; Gebicki and Maciejewska, 2003).



a) aqueous phase containing normal micelles

b) oily phase containing inverted micelles

Fig. 9. Typical micelle aggregate structures into which surfactants self-assemble in solution, (a) normal micelle with non polar tail of surfactant molecules in its interior, (b) inverted micelle with polar heads in its interior (Mortensen, 2001)

It can be also added that each structure may exist alone in a dominant aqueous or oily phase forming one phase (I or 1φ) or two phase (II or 2φ) according to the presence of two of them in equilibrium or one of them in equilibrium with either oil or water. Other options, that is an equilibrium of three phases (III or 3φ), are also possible.

The existence of pre-micelles, micelles, and liquid crystals of ionic surfactants depends not only on the surfactant concentration but also on the solution pH and inorganic ions concentration. Drzymala (1989) presented a diagram, containing different forms of oleate ions in water, at different pH values and Na^+ ions concentrations (Fig. 10).

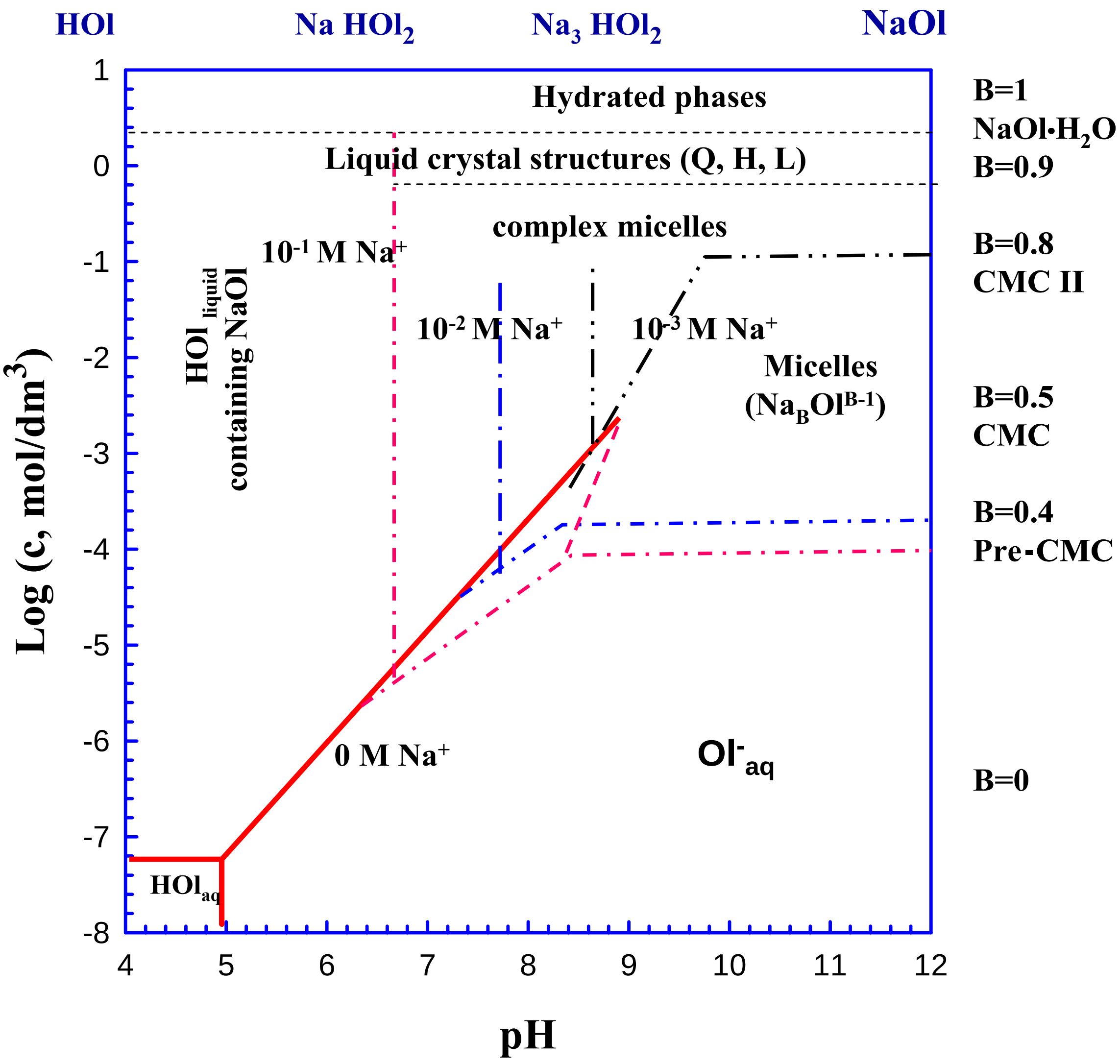


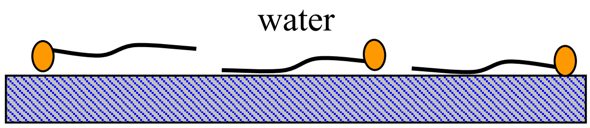
Fig. 10. Different forms resulted from varying surfactant (oleate) concentrations in water at different solutions pH and salt (sodium chloride) concentrations (after Drzymala, 1989). B expresses the stoichiemtry of oleate species

2.2.1.2. Flotation in the presence of surfactant solutions

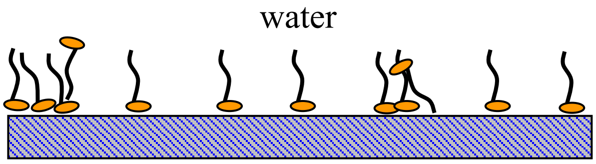
Surfactants interact with particles suspended in water. At very low concentrations, below CMC, the surfactant molecules adsorb at the solid/water interface mostly parallel to the hydrophobic particle surface (Fig. 11a). As concentration increases further, the adsorbed surfactant forms complex structures. They self-assemble at the hydrophilic solid sites of the particle surface to form two-dimensional analogues of the aggregating structures observed in the bulk solution, i.e. spherical or cylindrical surface micelles or bilayer-type structures (Lee et al., 1989;

Tiberg and Landgren; 1993; Heather et al., 2000, Tiberg et al., 2000). Fuerstenau and co-workers (Fuerstenau and Colic, 1999; Healy et al., 2003) called them hemi-micelles (Fig. 11b). A formation of a surfactant monolayer on the particle surface was also observed (Patrick et al., 1997) (Fig. 11c).

a) adsorption model from diluted surfactant solutions



b) adsorption model at higher surfactant concentrations



c) adsorption model at still higher surfactant concentrations

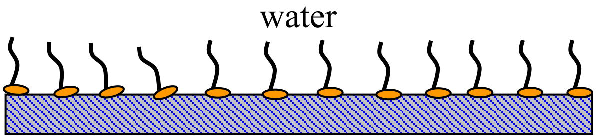


Fig. 11. Adsorption of surfactant at solid/water interface, a) at low concentration, b) at higher concentrations hemimicelles are formed, c) at still high concentration the formation of monolayer is possible (after Healy et al., 2003)

There is no a simple correlation governing flotation response and micelle formation in flotation solutions with surfactants as collectors (Dobias, 1986). For instance, Figure 12a shows that at concentration of sodium octadecyl sulfate (SOS) higher than its CMC, aluminum oxide recovery is still in an increasing order. On contrary, aluminum oxide recovery decreases at sodium dodecyl sulfate (SDS) concentrations higher than its CMC. Figure 12b confirms the same conclusion in the case of quartz flotation using cetylpyridinium chloride (CPC) as the collector. Case "1" in this Figure (without the addition of NaCl) shows a decrease of quartz floatability with CPC concentration higher than its CMC. Cases "2" and "3" of the same Figure (using 10^{-2} and 10^{-3} mol/dm^3 NaCl, respectively) reflect constant quartz floatability before and after CMC.

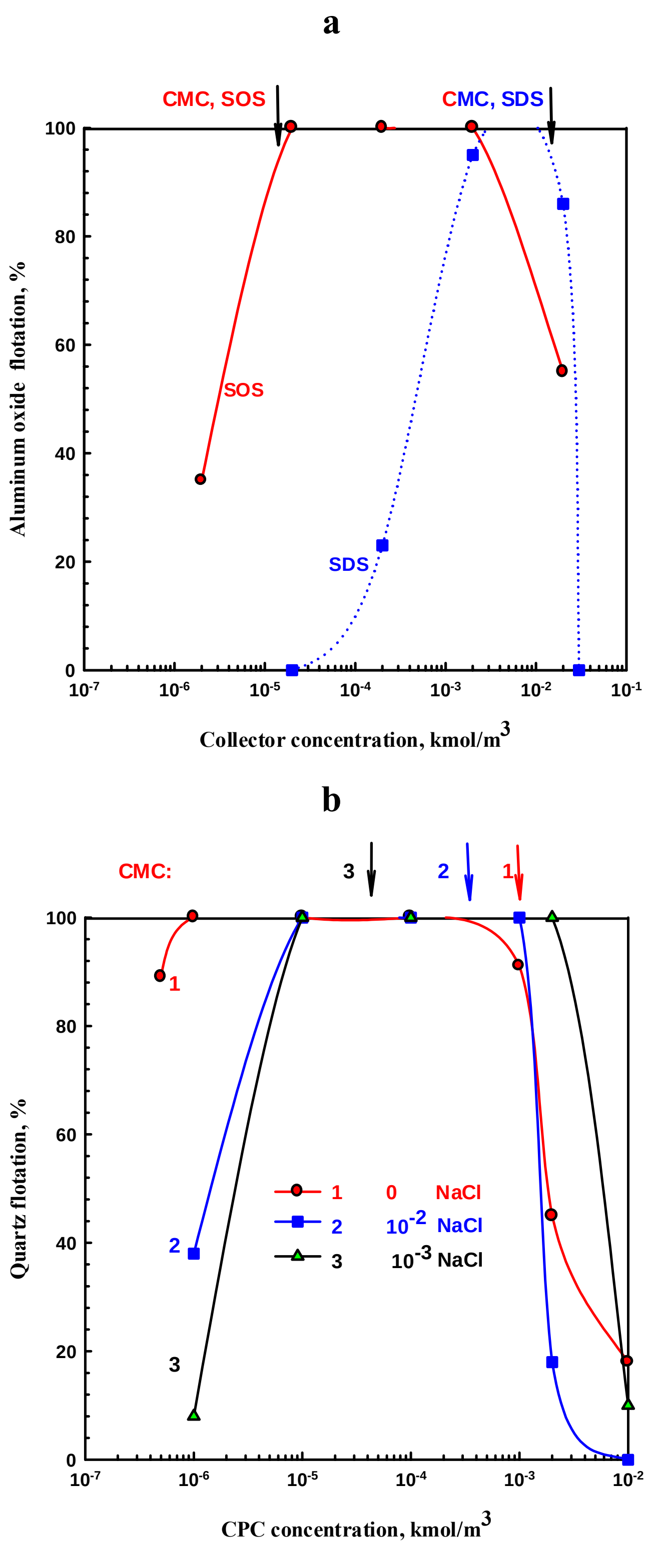


Fig. 12. Flotation studies for surfactant concentrations around CMC. Flotation of aluminum oxide using sodium dodecyl sulfate (SDS) and sodium octadecyl sulfate (SOS) (Freund and Dobias, 1995) (a). Effect of NaCl concentration on CMC and flotation of quartz at different concentrations of cetylpyridinium chloride (CPC) (Freund and Dobias, 1992) (b)

2.2.2. Aqueous emulsions

2.2.2.1. Properties

Flotation reagents are prepared by dissolution in water before they are introduced into the flotation cell. Certain flotation collectors, especially hydrocarbons and their derivatives (kerosene, crude petroleum, fuel oil, gas oil and certain coal-tar distillates, and many other oily reagents), are insoluble in water. Mixing them with water leads to dispersion, that is formation of tinny droplets in water, called emulsion. Emulsions are thermodynamically unstable. They can be stabilized either mechanically, by the use of surfactant, or with solid particles (Becher, 1977; Jones et al., 1978). The mechanical stabilization is realized by a mechanical or ultrasonic mixing (Sis and Chander, 2004), while the emulsion stabilization by the use of a surfactant is based on accumulation of surfactant molecules at the oil/water interface. It leads to:

a- decreasing the energy differences between the two phases and thus enhancing the stability of the aqueous emulsion (Georges and Desmettre, 1986)

b- changing the characteristics of the electrical double layer of the emulsion droplet leading to a reduction in the droplet/droplet coalescence by collision, and thus enhances the stability of the emulsion (Lucassen-Reynders and Kuijpers, 1992)

c- improving the droplet interface rheological properties by increasing its visco-elasticity enabling it to resist tangential stresses from adjoining liquids and standing for longer time.

The presence of ultrafine solid particles can also increase emulsion stability due to their accumulation at the oil/water interface (Polat and Chander, 1994b). Their accumulation creates a lack of droplet/droplet collision due to repulsive electrostatic forces (Forrest, 1990).

There are different types of emulsions (Ostwald, 1910). The oil-in-water (O/W) emulsion is characterized by small oil droplets dispersed in the water continuous phase (Fig. 13a). On the other hand, the water-in-oil (W/O) emulsion is encountered when small droplets of water are dispersed in an oily bulk phase (Fig. 13b). A third type, called multiple emulsion, is known to be either water-in-oil-in-water (W/O/W) (Fig.

13c) (Frenkel et al., 1983) or oil-in-water-in-oil (O/W/O) (Fig. 13d) (Distefano et al., 1983). Multiple emulsions appear when the formed droplet is coated with an outer shell. If an O/W droplet is coated with an outer shell of oil (or existed in a continuous oily phase), the oil-in-water-in-oil (O/W/O) multiple emulsion type will be created. In the case of the droplets of W/O included in a water larger droplet (or water continuous phase), the water-in-oil-in-water (W/O/W) multiple emulsion type is formed (Frenkel et al., 1983; Distefano et al., 1983; Magdassi et al., 1984). Figure 13 shows the types of emulsions.

It is interesting to add that the presence of an oil-in-oil (O/O) emulsion was claimed by Sharma, (1975). He was able to get droplets from benzene (oily phase) dispersed into a poly(ethylene glycol) ether using sodium dioctyl sulfosuccinate as a surfactant.

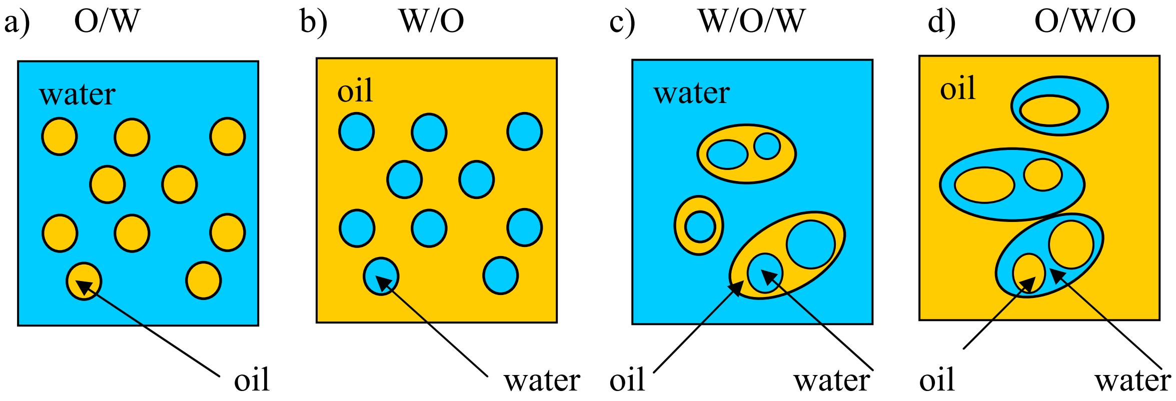


Fig. 13. Types of emulsions formed in water-oil systems and their droplet structure (based on different sources, see text)

The stability of emulsions seems to depend on the so-called hydrophobic-lipophilic-balance (HLB) of the surfactant used for stabilization (Ismail et al., 2001). Surfactants or mixtures of surfactants having the HLB in the range 3-6 will enhance the formation of W/O emulsions, while those with the HLB ranging 8-18 will help the formation of the O/W emulsions (Ismail et al., 2001).

The size of emulsion droplets depend on the preparation method. Figure 14 shows the average droplet size obtained during mechanical emulsification of a constant amount of dodecane in water applying different stirring speeds for different periods of time. The droplet size ranges from 12 to 130 μm and the median droplet size decreases with increasing stirrer speed and stirring time. According to Sis and Chander (2004), this is due to the increase of external stress on the droplets with the increasing energy consumption in the mixing process.

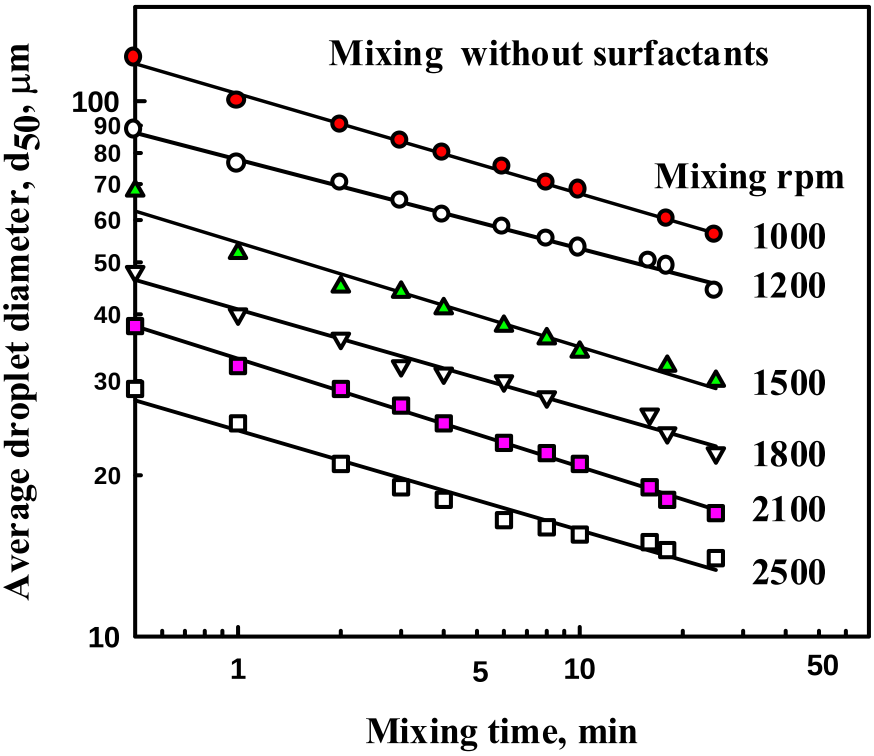


Fig. 14. Variation of median droplet size of 0.1% dodecane in water with mixing time and speed, rpm (revolution per minute) (after Sis and Chander, 2004).

Emulsification of the same amount of dodecane, in the presence of nonionic surfactants (Fig. 15), showed that a single line could not represent the variation of the median droplet size. Instead, the dispersion of dodecane was divided into two consequent regions along the time scale. Region I (adsorption region) is characterized by the adsorption of nonionic surfactant molecules at the dodecane/water interface and Region II (depletion region) is characterized by the depletion of surfactant molecules in the bulk due to adsorption at the dodecane/water interface (Fig. 15). The presence of a nonionic surfactant during the emulsification process leads also to a significant decrease in the size of dodecane droplet in water reaching a minimum of 6 µm.

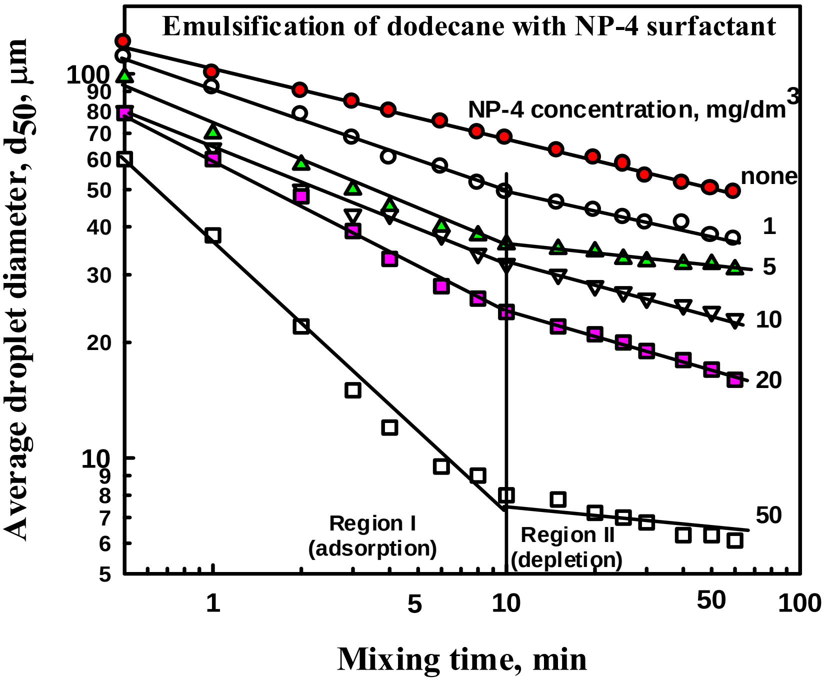


Fig. 15. Variation of median droplet size of 0.1% dodecane in water with mixing time and speed at the presence and absence of nonionic surfactants (after Sis and Chander, 2004), NP-4 (Tergitol) is nonylphenyl poly(ethylene glycol) ether having an average of four moles of ethylene oxide groups or shortly C_9phE_4

2.2.2.2. Flotation in the presence of aqueous emulsions

Application of emulsions as flotation collectors was considered by many workers (Mackenzie, 1969; Waksmundzki et al., 1975; 1976; Sotskova et al., 1988; Ofor, 1992; Polat et al., 1999; 2000). In flotation, the collector droplets collide with, adhere to, and spread on the coal particles to render them more hydrophobic (Bolat et al., 1998). The collector emulsification leads to a higher probability of collisions of mineral and oil particles (Moxon and Keast-Jones, 1986; Sis and Chander, 2004). It is expected also that the emulsification decreases collector consumption by introducing smaller droplets to the favored mineral site.

Polat and Chander (1994) suggested that wetting of the coal surface by collector droplets is a result of a complex mechanism. They observed, using high-speed photography, that the emulsion droplets were stabilized by high rank coal slimes. The slimes produced large oil-coal aggregates hampering flotation process. It was also shown, in full-scale industrial tests, that emulsification of oil with frother in the form of emulsions resulted in a significant improvement in the overall flotation results (Laskowski, 1993; Laskowski and Romero, 1996; Polat et al., 1999). Polat et al.

(2003) showed different associations between coal particles and oil droplets on different coal samples. They depicted that associations between coal particles and oil droplets depend on coal rank, oil concentration and the presence of surfactant. The possibilities are shown in Table 4.

Table 4. Association between coal particles and oil droplets as a function of coal rank, oil concentration and the presence of surfactant as well as its effect on flotation (after Polat et al., 2003)

Surfactant/oil usage	Coal Rank	Particle aggregation	Recovery	Selectivity	Surfactant effect
No surfactant and low amount of oil	high	small agglomerates	high	moderate	–
	low	no agglomerates	very low	low	–
No surfactant and high amount of oil	high	large size agglomerates (entrapment)	very high	low	--
	low	small size agglomerates	moderate	moderate	--
Surfactant and low amount of oil	high	moderate size agglomerates	high	high	surface modifier
	low	small size agglomerates	low	low	surface modifier
Surfactant with high amount of oil	high	moderate size agglomerates	moderate	moderate	modifier/ emulsifier
	low	small size agglomerates	high	high	modifier/ emulsifier

2.2.3. Mixed collectors

2.2.3.1. Properties

Mixing collectors in aqueous solutions, as a rule, changes their physical properties such as solubility and critical micelle concentration. When a new component is added, the adsorption of the first surfactant at the mineral/water interface changes. For instance, dodecyl alcohol is not adsorbed on the quartz surface. However, its adsorption appears in the presence of a cationic dodecyl amine (Smith, 1963). Studies showed that interactions among collector mixtures depend on different factors including nature, concentration and type of the mixed collectors (Shimoiizaka et al., 1976), nature and surface charge of minerals (Rao and Frossberg, 1993), in addition to factors related to the nature and interactions taking place in the aqueous phase (Helbig et al., 1998). Helbig et al. (1998) suggested a model for collector mixtures interaction in a flotation system. Their model takes into consideration the formation of different species in aqueous solutions (Fig. 16) including:

a- formation of a mixed film at the liquid–gas interface leading to a rapid decrease of the surface tension (Schwuger, 1971)
b- formation of mixed micelles which cause CMC shifts to lower concentrations (Jost et al., 1988)
c- precipitation of collector molecules by multivalent cations (Morozov et al., 1992)
d- interaction between differently charged surfactant ions, if any, leading to the formation of insoluble complexes (Helbig et al., 1998).

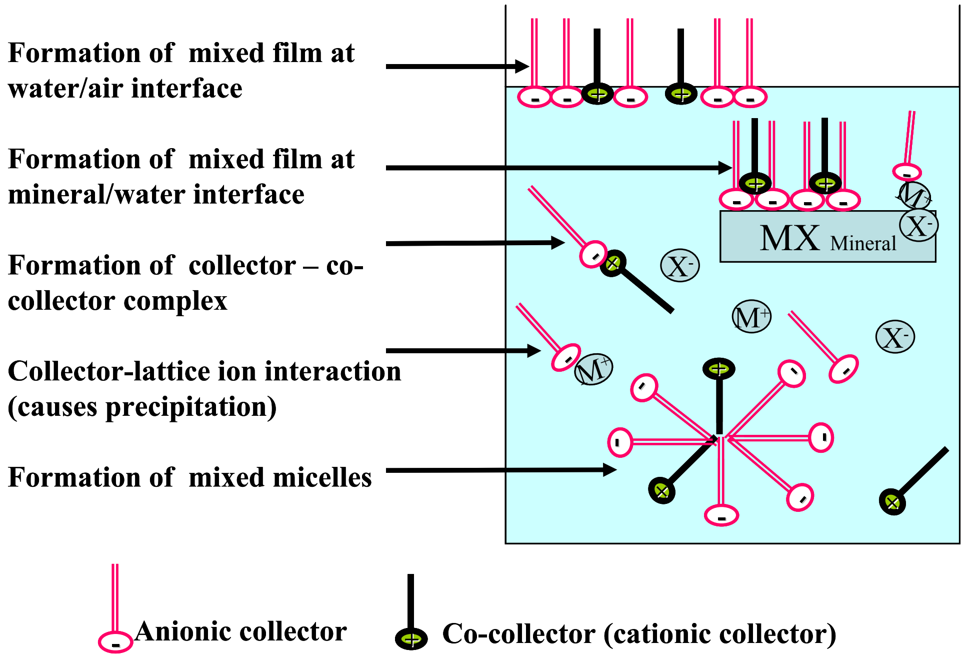


Fig. 16. Possible interactions in a mixture of collectors in flotation (after Helbig, et al. 1998)

2.2.3.2. Flotation in the presence of mixed collectors

Collector mixtures including cationic surfactants/anionic surfactants, ionic surfactants/nonionic surfactants, oils/ionic surfactants, and oils/nonionic surfactants improve flotational separation (von Rybinski and Schwuger, 1986; 1987; Rao et al., 1988; 1990(a-b); Rao and Frossberg, 1991; 1993; 1995; 1997). For instance, Figure 17a shows that the fluorite recovery was improved from initial 20% using dodecylammonium chloride (C_{12}amine or $C_{12}H_{25}$-NH_3Cl) collector alone to 87% as the collector was mixed with sodium *N*-dodecanol sarcosinate (shortly C_{12}sarcosine or $C_{11}H_{23}CON(CH_3)CH_2COONa$). At the same time, Figure 17b shows that the fluorite recovery reached 62% when the dodecylammonium chloride (C_{12}amine, $C_{12}H_{25}$-NH_3Cl) collector was mixed with sodium dodecanate (C_{12}acid, $C_{11}H_{23}COONa$). This is attributed to the mutual interactions taking place between the mixed collectors (Helbig et al., 1998).

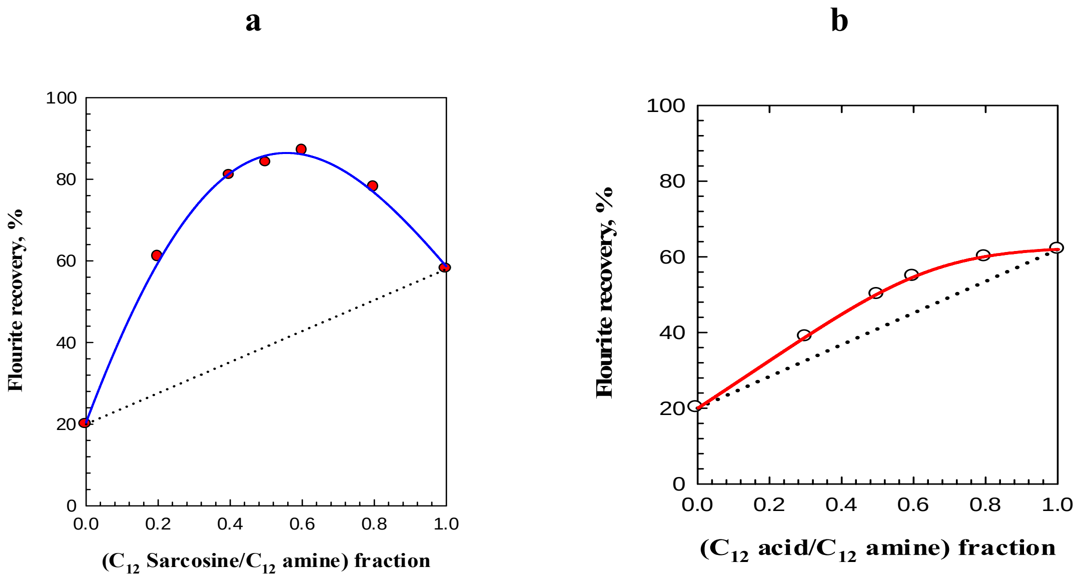


Fig. 17. Effect of mixing collectors on fluorite flotation, (a) C_{12} amine mixed with C_{12} sarcosine at total concentration of $3{\cdot}10^{-5}$ kmol/dm^3, (b) C_{12} amine together with carboxylic acid at total concentration of $6{\cdot}10^{-6}$ kmol/dm^3 (Helbig et al., 1998)

Mixtures of cationic alkyl trimethyl bromide (TAB) and anionic xanthate applied to separate quartz from sulfide minerals (sphalerite, pentlandite and pyrrhotite) (Buckenham and Schuman, 1963) showed an optimum xanthate/TAB ratio for separation. Katayanagi (1974), in his patent, showed that the use of mixed anionic/cationic collectors for feldspar/quartz separation in an acidic circuit (at pH = 2) was successfully applied. The effect of using fatty acid amine acetate (Armac T) as cationic collector mixed with sodium petroleum sulfonate (Reagent 308) as anionic collector was studied in another series of flotation tests to separate alkali feldspars and heavy minerals from quartz (McEwen et al., 1976). The best separation was achieved at an optimum cationic/anionic collector ratio of 0.5. This was attributed to the neutralizing effect in the combined collector system in addition to the formation of stable complexes of both collectors. Also, diamine/sulfonate (cationic/anionic) mixtures provided successful flotation of feldspar minerals from natural silica at natural pH values (Jiaying et al., 1988; 1993). Alkyl diamine/C_n-dioxyethelene sulphate (cationic/anionic) mixtures reflected an optimal ratio suitable for microcline flotation, that is at the alkyl C_n-dioxyethelene sulphate/diamine ratio of 0.25-0.66 (Rao and Frossberg, 1993). The same authors declared a general rule that the anionic/cationic collector molar ratio in mixed collector flotation should be less than unity (Rao and Frossberg, 1995). They stated "*In general, when the mole ratio exceeds unity, flotation decreases either due to neutralization and the formation of nondissociating complex or due to the adsorption of excess anions in reverse orientation.*"

In another category, anionic/nonionic mixed collectors in flotation systems have been investigated. The ionic tall oil (mixtures of fatty acids) combined with nonionic nonylphenyl tetraglycol ether (C_9phE_4) was used to investigate apatite flotation from a phosphorite ore containing dolomitic calcite (Lovell, 1976). The apatite separation was successfully achieved and related to the improved froth characteristics caused by the nonionic reagent. The usage of $2.3 \cdot 10^{-5}$ M dodecyl alcohol mixed with 10^{-5} M sodium dodecylsulfate at pH 6 increased corundum recovery up to 90% (Fuerstenau and Yamada, 1962). The improvement was attributed to the co-adsorption of dodecyl alcohol neutral molecules with the collector molecules.

The effect of sulfosuccinate (anionic collector) and nonionic alkyl poly(ethylene glycol) ethers (C_xE_y) mixed collector on flotation of cassiterite from its synthetic mixture with quartz as well as from natural cassiterite ore was investigated by Doren et al. (1979). First, none of the reagents have collecting properties towards cassiterite and quartz, but the use mixture of the two reagents improved the selectivity and recovery of cassiterite only. The use of various alkyl poly(ethelene glycol) ether compounds mixed with fatty acids for fluorite flotation from a dolomite/calcite ore at a constant fatty acid level indicated an increase in fluorite recovery but not selectivity (Giesekke and Harris, 1984). For the same flourite recovery and grade, the required amount of fatty acid decreased 25-45% by the use of alkyl poly(ethelene glycol) ether compounds. This result was explained by the fact that the fatty acid presence enhances co-adsorption of alkyl poly(ethelene glycol) ethers on fluorite surface. Mixed anionic/nonionic collectors were also used in flotation of scheelite from the ore containing calcite (Rybinski et al., 1987). The results showed an increase in the selectivity of flotation.

Anionic/anionic (oleate/ethoxylated-sulfonate) collector mixtures were used successfully for flotation of mixed francolite and dolomite (Somasundaran et al., 1991).

In addition, there are many published papers illustrating positive flotational separation due to interactions of mixed collectors in flotation. Table 5 shows more than hitherto presented examples of application of different mixed collector in flotation.

Table 5. Mixed collectors applied for ores flotation

Collector	Co-collector or (promoter)	Ore or mineral mixtures	Reference
Sodium sulphosuccinate	Octylphenol ethoxylates	Cassitterite	(Doren et al., 1979)
Amine (Armak T)	Fuel oil	Phosphate ore	(Karjalahti, 1972)
Oleic acid	n-Hexadecane	Ilmenite	(Gutierrez, 1977)
Sodium petroleum sulfonate (Reagent 308)	Fatty acid amine acetate (Armac T)	Alkali feldspars and heavy minerals	(McEwen et al., 1976)
Sodium alkyl sulfates	Sodium alkyl sulfonates	Anatase and hematite	(Fuerstenau and Colic, 1999)
Fatty acids	Alkylphenol ethoxylates	Fluorite ore	(Giesekke and Harris, 1984)
Fatty acids	Alkylphenol ethoxylates	Phosphate ore	(Giesekke and Harris, 1994)
Fatty acid	Fuel oil mixed with polyglycols	Phosphate ore	(El-Shall et al., 2000)
Fatty acid	Fuel oil and sodium alkyl ether sulfate	Phosphate ore	(El-Shall et al., 2000)

Table 5 (cont.). Mixed collectors applied for ores flotation

Collector	Co-collector or (promoter)	Ore or mineral mixtures	Reference
Fatty acids	Tween 80	Fluorite and apatite	(Lu et al., 1997b)
Fatty acids	Amphoteric surfactants	Phosphate ore	(Lu and Sun, 1999)
Fuel oil	Oleic acid and mixture of diesel oil, acetic acid, and a proprietary alkanolamide (DOW M210)	Unburned carbon from fly ash	(Eisele and Kawatra, 2002)
Kerosene	Acorga m5640 + flotigol cs	Coal (lignite)	(Cebeci, 2002)
Fatty acids	Polyethoxy ethylene and polyprpolene polymers	Phosphate ore	(Lu et al., 1999)
Kerosene + iso-octanol	Semi-oily pitch	Coal	(Atesok and Celik, 2000)
Sodium isopropyl Xanthate	Sodium hydrosulphide	Sulphide ore (Chalcopyrite and Chalcocite)	(Chabuka and Witika, 2001)
Sodium oleate	Sulfosuccinate and sulfosuccinamate	Apatite	(Pinto et al., 1991)
Triton X-100	MIBC and Brij 35	Coal	(Murat et al., 2003)
Potassium oleate	Ethoxylated sulphonates	Apatite and dolomite	(Somasundaran et al., 1991)
Tall oil	Pamak 1and Pamak 4	Coal	(Sis et al., 2003)
Sodium oleate	Octylphenol ethoxylates	Feldspar	(Salmawy, 1997)
Sodium oleate	Nonylphenol ethoxylates	Phosphate ore	(Sis and Chander, 2000)
Kerosene and fuel oil	Dialkylthionocarbamate (Dow Z-200)	Copper and Molybdenum ores	(Harris and Jia, 2000)
Sodium sarcosinate	Alkylphenol ethoxylates	Phosphate ore	(Buttner et al., 1991)
Dodecanoyl sarcosine	Alkylammonium chlorides	Fluorite	(Helbig et al., 1998)
Sodium sulfosuccinamate	Aliphatic isoalcohol (Exol-B)	Cassiterite	(Filippov and Houot, 1997)
Alkyl sulfosuccinate	Alkylphenol ethoxylates	Scheelite	(Rybinski et al., 1987)
Fatty acids	Alkylphenol ethoxylates	Phosphate ore	(Lovell, 1976)
Fatty acids	Fuel oil	Phosphate ore	(Giesekke, 1985)

It can be concluded that application of more than one collector is usually beneficial for flotation. The adsorption of mixed collectors on the solid/water interface is a complex phenomena resulted from different interactions. The interactions may be simple taking place between two elements of the flotation system for example collector/co-collector, collector/water, mineral/water, mineral/collector or sometimes complex occurring among three elements or more as water/collector/mineral or mineral/water/collector, mineral/water/collector/co-collector etc. One can imagine that such interactions can be controlled if the considered collectors were introduced into the flotation cell as emulsions or microemulsions.

2.2.4. Special case of mixed collectors: microemulsions

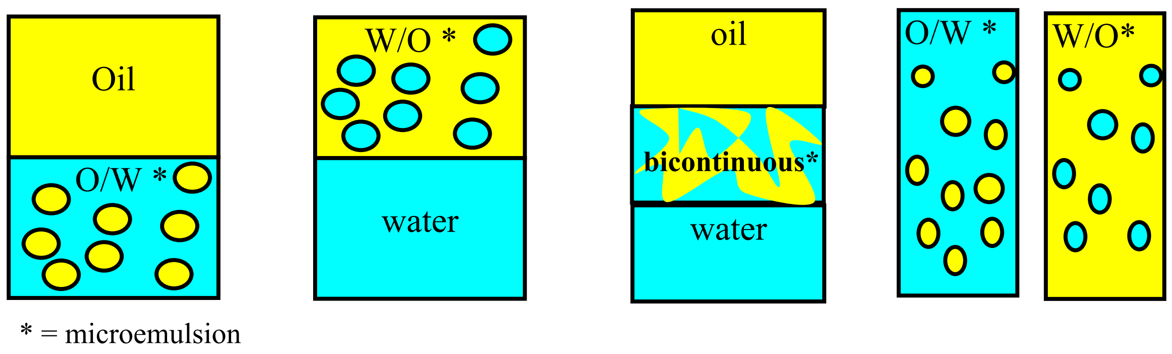
2.2.4.1. Microemulsions

Microemulsions are special emulsions which are transparent. Similarly to emulsions, they consist of one or two surfactants, oil, and water. However, the average droplet size of microemulsions can be in the range of 5 - 100 nanometers (nm) while it can be up to hundreds of microns for emulsion droplets (Overbeek et al., 1984; Huibers, 1996). Microemulsions show both kinetic and thermodynamic stability and hence they can be spontaneously formed (Overbeek et al., 1984; Vollmer and Vollmer, 2001). Therefore, a mixture of a right composition of water and a surfactant (sometimes another surfactant called co-surfactant), as well as oil may spontaneously homogenize itself forming microemulsion. The co-surfactant is usually a short chain alcohol ranging from two (ethanol) to four carbon atoms (butanol) (Huibers, 1996). The use of other alcohols, up to twelve carbon atoms (decanol) (Zecchino et al., 1991), and alkyl poly(ethylene glycol) ethers (Mutasem et al., 2002), was studied as the co-surfactants.

Similarly to emulsions, microemulsions can be oil-in-water (O/W microemulsion) or water-in-oil (W/O microemulsion) (Winsor, 1954). The W/O microemulsion is similar to reverse micelles, where the amphiphile molecules (the polar heads) of the surfactant are oriented inward and the non polar tails oriented towards the oil continuous phase. The main difference that distinguishes water/oil microemulsions from micellar solutions is the presence of free water in the core of a microemulsion droplet leading to a larger droplet size in the case of microemulsion (Moulik and Paul, 1998). The size of reverse micelles is usually restricted within 5 nm while greater size changes the status of the reverse micelle to microemulsion (Leung and Shah, 1986). On the other hand, normal micelles can consume oil and grow in size resulting in O/W droplet type microemulsion. Therefore, microemulsion droplets have uniform sizes when they are near their original micelles. In the case that O/W microemulsion type forms a single phase, it is also called Winsor IV (A) while the W/O single phase microemulsion is termed Winsor IV (B) (Fig. 18d).

In some cases, O/W microemulsions coexist with excess oil forming two-phase system. It is named in literature Winsor I (Fig. 18a). The system having W/O microemulsions in equilibrium with excess water is called in literature Winsor II (Fig. 18b). Winsor III (Fig. 18c) represents the three-phase system containing intermediate or non-droplet type microemulsion, where both oil and water present in a continuous form in the middle phase, which is in equilibrium with an upper oily phase and lower aqueous phase.

Conversion between one, two, and three phase system containing microemulsion may take place by adjusting the proportion of components in the system.



a) Winsor I
(two phases, O/W microemulsion phase in equilibrium with oil phase)

b) Winsor II
(two phases, W/O microemulsion phase in equilibrium with water phase)

c) Winsor III
(three phases, oil, bicontinuous, and water)

d) Winsor IV
(one phase, may be either O/W or W/O microemulsion phase)
O/W (A) W/O (B)

Fig. 18. Microemulsions, a) and b) represent two-phase system containing microemulsion, c) three-phase, and d) one-phase microemulsion system (after different sources, see text)

The ternary mixtures of water-surfactant-oil or quaternary mixtures of water–surfactant–co-surfactant–oil can have different characteristic structures that are surfactant solutions, emulsions, and microemulsions. The structures, resulted from the ternary or quaternary systems, are usually illustrated using phase diagrams. A phase diagram depicts different possible ratios of components and the formed structures.

Figure 19 shows a typical phase diagram with different expected structure areas in a water–oil–surfactant/s system.

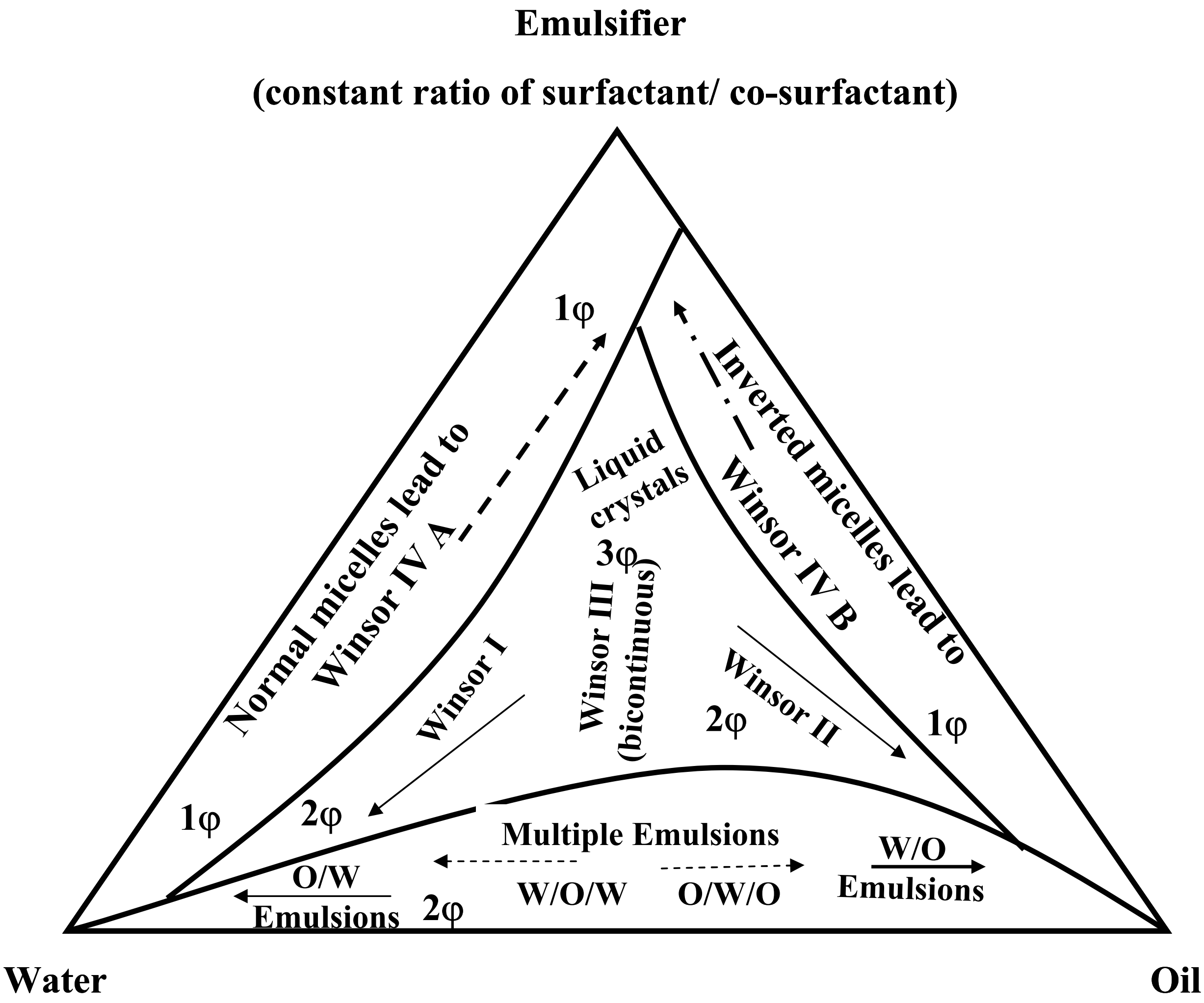


Fig. 19. A phase diagram of water-oil-emulsifier system (after Prince, 1975), W stands for water, O for oil, while 1φ, 2φ, and 3φ refer to one-phase, two-phase, and three-phase systems

It can be seen from Fig. 19 that the O/W emulsion exists at the water rich region while W/O usually appears at the oil rich corner. Multiple emulsions exist in the intermediate region. Normal and inverted micelles appear at the surfactant-water or surfactant-oil borders, respectively, and extend to the interior of the phase diagram. Different types of microemulsions are encountered in the center of the phase diagram (Winsor I-III). Data from Fig. 19 are shown again in a pictorial form in Fig. 20.

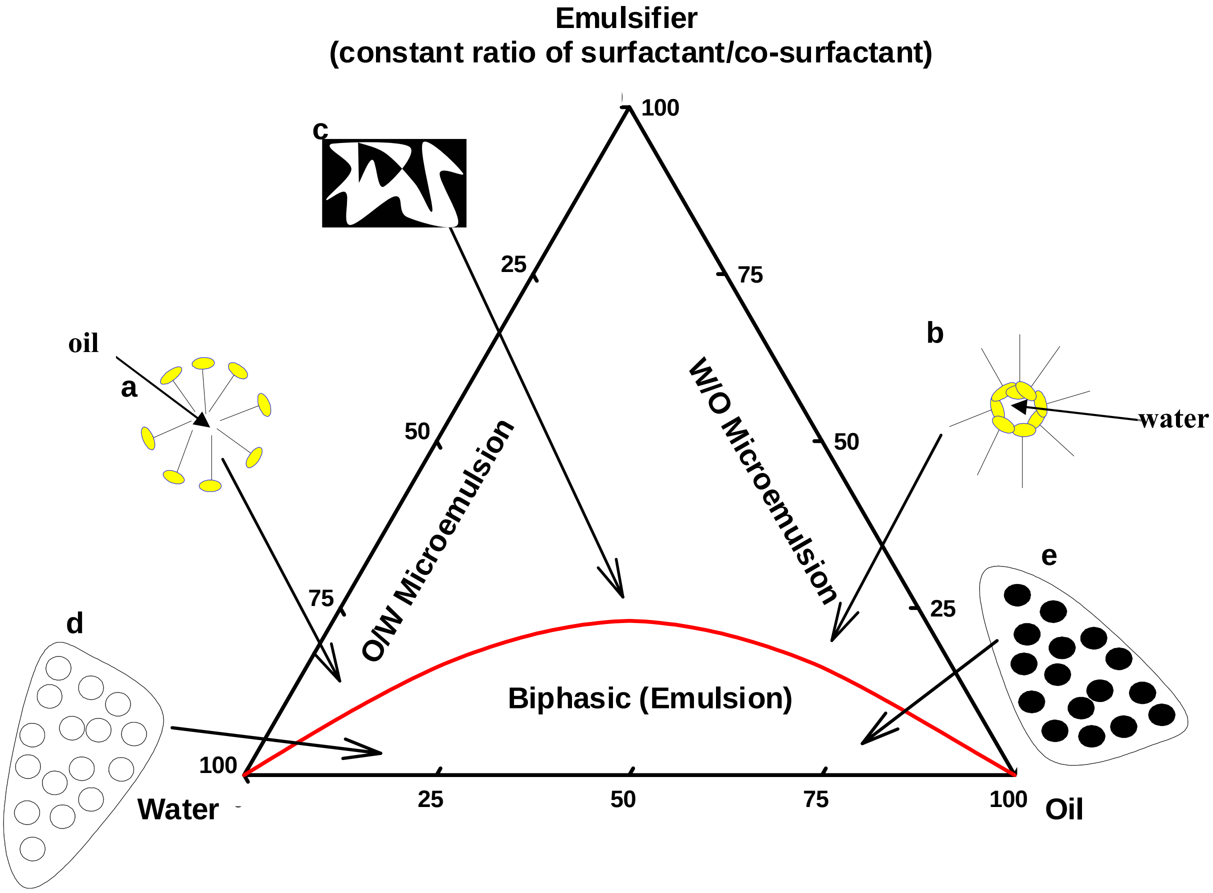


Fig. 20. Schematic ternary phase diagram showing structures encountered in the system, a) O/W microemulsion droplet, b) W/O microemulsion droplet, c) bicontinuous dispersion structure, d) isolated and aggregated O/W droplets, and e) isolated and aggregated W/O droplets

Sometimes, a disappearance of one or more areas is possible. Figure 21 shows actual phase diagrams from literature containing different typically encountered areas.

An important factor in the microemulsion formulation and structure is the type of surfactant. When surfactant is the only factor controlling microemulsion formulation and structure (i.e. the system is co-surfactant free), there are three conflicting concepts that must be considered simultaneously (Abe et al., 1986):

a- surfactant must partition equally between the oil and water phases, through optimization of temperature, surfactant hydrophilic group structure, surfactant hydrophobic group structure, oil phase composition, and electrolyte composition in the aqueous phase b- surfactant molecules must reach maximum linear extension, to produce high solubilization and low interfacial tension. Surfactant concentration must be above the critical micelle concentration

c- net surfactant lateral interactions must be weak. The system must be above the melting point of all extended structures, such as liquid crystals and gels, so that the microemulsion state will be thermodynamically most stable.

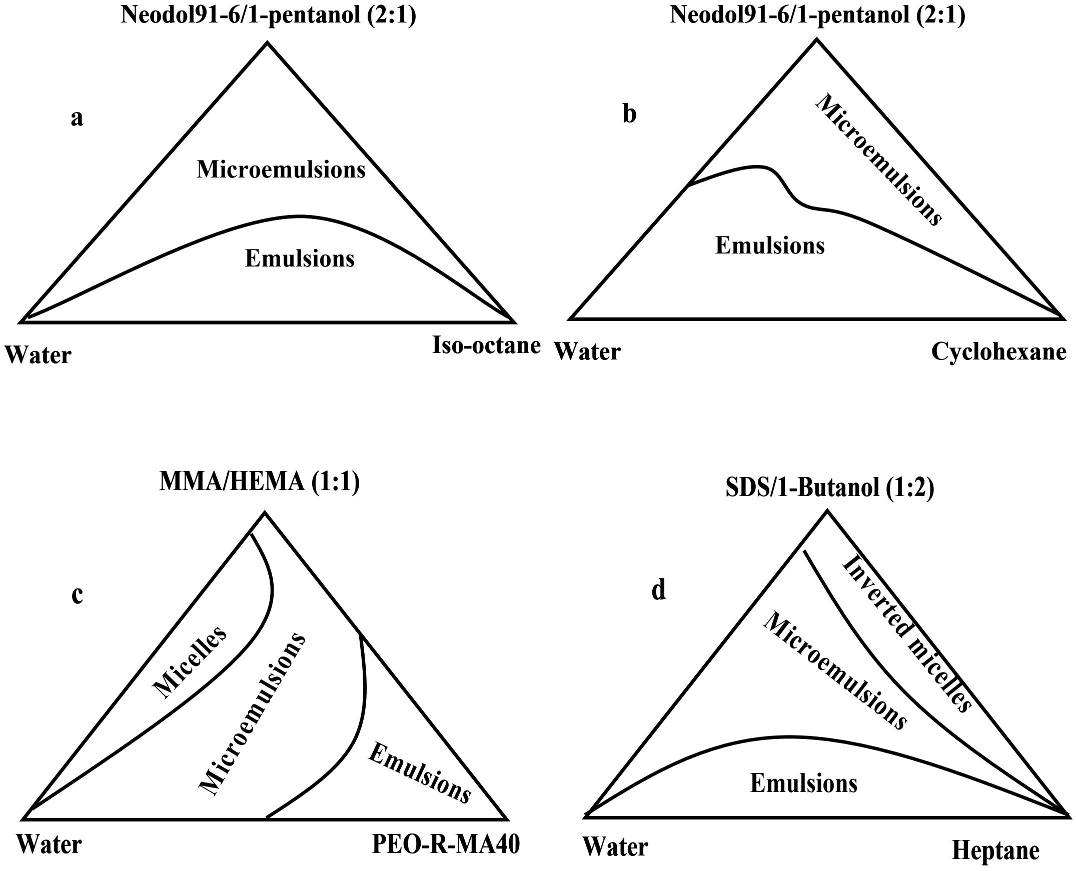


Fig. 21. Phase diagrams showing disappearance of certain structures, a) and b) (after Zarur et al., 2000), c) (after Gan et al., 1997), d) after (Watarai, 1997). Acronyms for the used chemicals are: Neodol91-6 = $C_{10}E_6$, SDS=sodium dodecyl sulfate, MMA = methyl methacrylate, HEMA = 2-hydroxyethyl methacrylate, PEO-R-MA40 =ω-methoxy poly(ethylene oxide)$_{40}$ undecyl-α- methacrylate

Abe et al., (1986) recommended the following advices to achieve the above requirements:

1- shortening hydrophobe length and increasing hydrophobe branching
2- adding ethylene oxide units
3- increasing temperature and decreasing electrolyte concentration.

2.2.4.2. Microemulsions in mineral processing and other applications

There seems to be no reported applications of microemulsions in mineral processing. A closer look into microemulsions shows that they consist of all components needed for flotation of materials. They contain two collectors (oil and surfactant or co-surfactant), frother (co-surfactant or surfactant), and water. It is expected that microemulsions can be used in flotation. Therefore, the application of microemulsions in flotation of difficult-to-float oxidized coal will be tested in this thesis. The idea propagates also from the fact that flotation of hydrophilic minerals requires changing their surface properties to hydrophobic. This takes place by using collectors. A classical way of enhancing collector selectivity is using activators which not always provide satisfactory results. Another approach is using an additional collector as a mixed collector system. This additional collector may be oil (Boteva, 1996) or another collector (Rao and Forssberg, 1995). The use of mixed-collectors in flotation systems was reviewed by Rao and Forssberg (1997) and was discussed before in this thesis.

Besides the possible application of microemulsions in mineral processing, there are many other areas for utilization of microemulsions. For example, microemulsions can be used in artificial blood composed of fluorocarbon oil-in-water, which is capable of storing oxygen and release it in the presence of carbon dioxide. Since the diameter of the droplet of the microemulsion is less than 100 nanometers, it makes the liquid practical, because it can pass through the capillaries and thus system can pass through human viens (Moore et al., 1996). Creation of fuel-water stable microemulsion was patented in the early 1970's. One of the direct advantages of such fuel microemulsion system is its water content, where water is vaporized during the combustion process lowering the heat of combustion and thus reducing the release of NO_x and CO gases. Ahmed and Drzymala (2003) discussed many other applications of microemulsions.

2.3. Flotation of difficult-to-float materials

Application of flotation for upgrading of many ores and raw materials is highly successful because they can be processed by using suitable collector-frother systems (Jameson et al., 1977; Trahar, 1981). However, some minerals experience problems during their flotation. They either do not adsorb collectors or their flotation is highly unselective. Such solids are called difficult-to-float materials (Reay and Ratcliff, 1973; Collins and Jameson, 1976; Bustamante and Warren, 1984).

Low rank and oxidized coals, especially lignites, are among the most difficult to float materials (Aplan, 1983; 1993; Bolat et al., 1998). For instance, investigations showed that laboratory oxidation of bituminous coal causes a flotation yield drop from an initial 95% down to 24% using alcohol type frothers (Sarikaya, 1995). This poor flotation response of oxidized coal has been mainly attributed to physical and chemical adsorption of oxygen on its surface forming polar phenol (–OH), carbonyl (=C=O), and carboxyl (–COOH) groups (Schlyer and Wolf, 1981; Somasundaran et al., 1991, 2000). The groups enhance surface hydration and hydrophilicity preventing typical non polar flotation reagents from being adsorbed at the surface (Tekely et al., 1987; Ramesh and Somasundaran, 1989). In addition, they form humic acids, which then degrade into soluble acids (Fuerstenau et al., 1987) that have significant negative impacts on surface charge, which controls reagents adsorption and film-thinning process, and thus flotation kinetics and outputs (Miller, 1977; Fuerstenau et al., 1983; Miller et al., 1983).

Different approaches are used for improvement of flotation of difficult-to-float materials. These approaches were discussed by Ahmed and Drzymala (2004; 2005) and will be shortly reviewed here. The first approach stressed cleaning the surface of particles to remove surface-harmful groups. It was achieved by applying long-term conditioning at a high solid/liquid ratio (up to 20 min at 1600 rpm with 65% solids, Chander et al., 1995; Vamvuka and Agridiotis, 2001) and/or by ultrasonic treatment (Buttermore et al., 1991). Sonication of coal treated with reducing agents prior to flotation completely restored its hydrophobicity. Under appropriate conditions, 50% reduction in collector consumption was achieved due to surface cleaning by ultrasonication (Celik, 1989). Surface cleaning was also carried out chemically by using reducing agents such as hydrazine (Majka-Myrcha and Girczys, 1993). They increased the yield of an oxidized-coal from 20% to about 95% when flotation was carried out in a 10% hydrazine solution.

Other investigations paid attention to addition of electrolytes during coal flotation (for summary see Ratajczak and Drzymala, 2003). It appears that flotation of coal can be improved in saline waters. It is also known that coal flotation at low electrolyte concentrations decreases but increases at high electrolyte concentrations (Laskowski, 1963; Paul et al., 2002; Ratajczak and Drzymala, 2003). The most likely mechanisms by which electrolytes affect coal flotation is that electrolyte adsorption makes the coal surface hydration layer less stable (Laskowski, 2001). In addition to that, electrolytes seem to enhance the presence and stability of microbubbles at the coal surface (Paul et al., 2002). According to Ratajczak and Drzymala, (2003) salt flotation is possible only with salts having surface energy greater than that of water (72.8 mJ/m^2).

Another trial to improve flotation of difficult-to-float materials is based on switching from non polar oily collectors to nonionic and ionic surfactant collectors (Aplan and Arnold, 1991; jia et al., 2000). The approach takes advantage of the fact that the surface charge of unoxidized and oxidized coal samples depend on pH and oxidized coal is negatively charged above pH $\approx$ 2, while the collector is positively charged (Bolat et al., 1998). Bustamante and Woods (1984) used dodecylamine as a cationic collector and were able to achieve high flotation yields of coal at pH below 6. Anionic collectors such as sodium dodecyl sulphate (Crawford and Mainwaring, 2001), tributyl phosphate, and carboxylic acids (Aplan and Arnold, 1991) were also successfully used. The use of oxygenated functional groups in a nonionic molecule of collector [alkyl poly(ethylene glycol) ethers] was found to have a positive effect on flotation of low rank and oxidized coals (Wojcik et al., 1989, 1990; Chander et al., 1994, Jia et al., 2000). Also long chain alcohols with aromatic rings, for instance nonyl benzene, was found to be a better collector for oxidized coal flotation than dodecane due to a strong interaction of the rings with aromatic sites on the coal surface (Harris, 1995).

Some other improvement projects paid attention to reagents types and their simultaneous mixtures (Laskowski and Miller, 1984; Onlin and Aplan, 1987; 1989; Laskowski, 1993; Laskowski and Romero, 1996; Drzymala et al., 2005). The results showed that mixtures of reagents usually improve flotation. For instance, the use of light and heavy oil mixtures has been found to improve the flotation of a low-rank coal (Ghiani et al., 1989). Other recommendations include the use of a main collector with additional collector called "co-collector or promoter" (Sablik, 1984; Saleh and Iskra, 1997b; Polat and Chander, 1998, 1999; Polat et al., 1994b; Celik and Seyhan, 1995). According to Sablik (1998), the goal is to alter the hydrophobicity of difficult-to-float coal by co-adsorption of the promoter. He showed that the surfactants used as promoters are usually nonionic polyglycol ether type compounds. They had double effect on flotation. They modified the coal surface and also improved the emulsification of the collector. It was also found that the co-adsorption of such surfactants at the solid/liquid interface influences the hydrophobicity of solids by altering the surface free energy of the solid–liquid interface. Presently, numerous literature examples showing the application of promoter-collector approach are available. For example, Vamvuka and Agridiotis (2001) observed a superior separation when a combination of kerosene and dodecylamine were utilized. Strydom et al. (1983) have also employed a promoter–alcohol mixture, that is sodium di-isobutyl sulfosuccinate with methyl isobutylcarbinol (MIBC), and obtained a certain recovery and grade at a much lower reagent dosage than with MIBC alone. Also blends of hydrocarbons and various copolymers, long chain amines and fatty acid amides, improve flotation of difficult-to-float materials (Majka-Myrcha and Sobieraj, 1987; Moxon et al., 1988; Chander et al., 1996). In addition, the use of oils and ionic or nonionic surfactants as mixtures of reagents to enhance flotation of coal and other mineral commodities is well documented in literature (Moxon et al., 1988; Vamvuka and Agridiotis, 2001; Murat et al., 2003).

Mixed reagents simultaneously with added electrolytes were tested by Lu et al. (1999). They concluded that the tolerance of oleate to pH variation and presence of the Ca^{+2} ions increased in the presence of a nonionic polymer. Another investigation conducted by Lovell (1976) showed that the presence of solid particles (e.g., apatite and calcite) prevented froth formation when fatty acids were used alone, but the presence of a nonionic surfactant (nonylphenyl tetraglycol ether) improved the froth formation, which is very essential in froth flotation.

3. Graphical representation of experimental results

3.1. Introduction

Dealing with many variables and responses of investigated systems always creates problems regarding suitable graphical representation of the data. For this reason, this chapter is designed to discuss graphical representation of results starting from one variable and a response and ending with more complex cases that cover interests of this thesis. It is an extension of a work initiated by the author of this thesis in 2004 (Ahmed, 2004).

3.2. One variable

This is the simplest case in which variable (A) is independent, as its values or levels (a1, a2, etc.) can be freely changed or selected. Different plots, for a hypothetical flotation system affected by one variable (A) providing one response (R), are shown in Fig. 22a-d. Figure 22a is a simple two-dimensional (2D) cartesian plot where the variable is represented on one axis (x-axis) having unlimited scale, while the flotation response is shown on the other axis (y-axis), which also has an unlimited scale. This plot can be called the full plot because all elements of the system (variable and response) are presented in the graph axes. In this full plot (Fig. 22a), the lines parallel to the response axis show a constant level of the variable, while lines parallel to variable axis are called the iso-response lines. Figure 22b is a one-dimensional (1D) response (linear) plot representing the same situation shown in the full plot but with the projection of the response values (V) on the variable axis. Thus, the values of the response (V_{a1}, V_{a2}, etc.) can be written at each corresponding studied level of the variable (a1, a2, etc.). It should be mentioned that the linear plot together with the response values and other descriptions in fact form a 2D graphical representation of the upgrading results. A side view of the linear plot (Fig. 22b) can lead to a zero-dimensional (0D) point plot shown in Fig. 22c. It shows a point (0D) having (2D) information regarding the levels of the variable and the corresponding separation response values. The point plot (Fig. 22c) is very similar to a data table form where the data are mentioned in an ordered manner (Fig. 22d, table plot). The table plot can assume different forms depending on the table format as well as number of rows and columns.

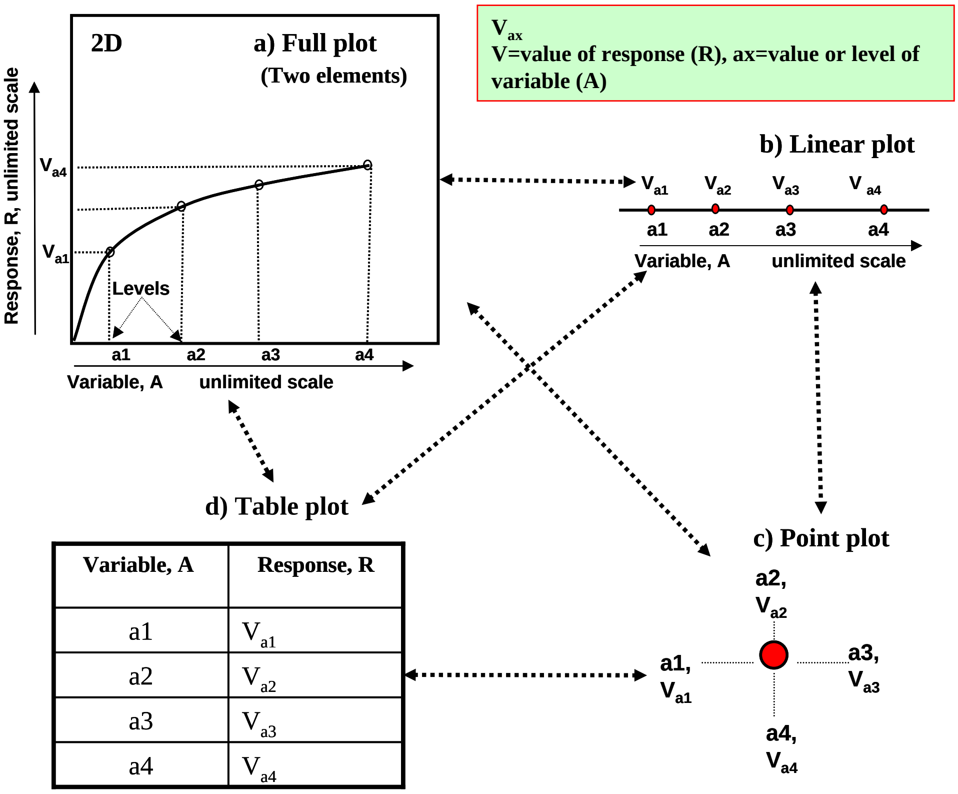
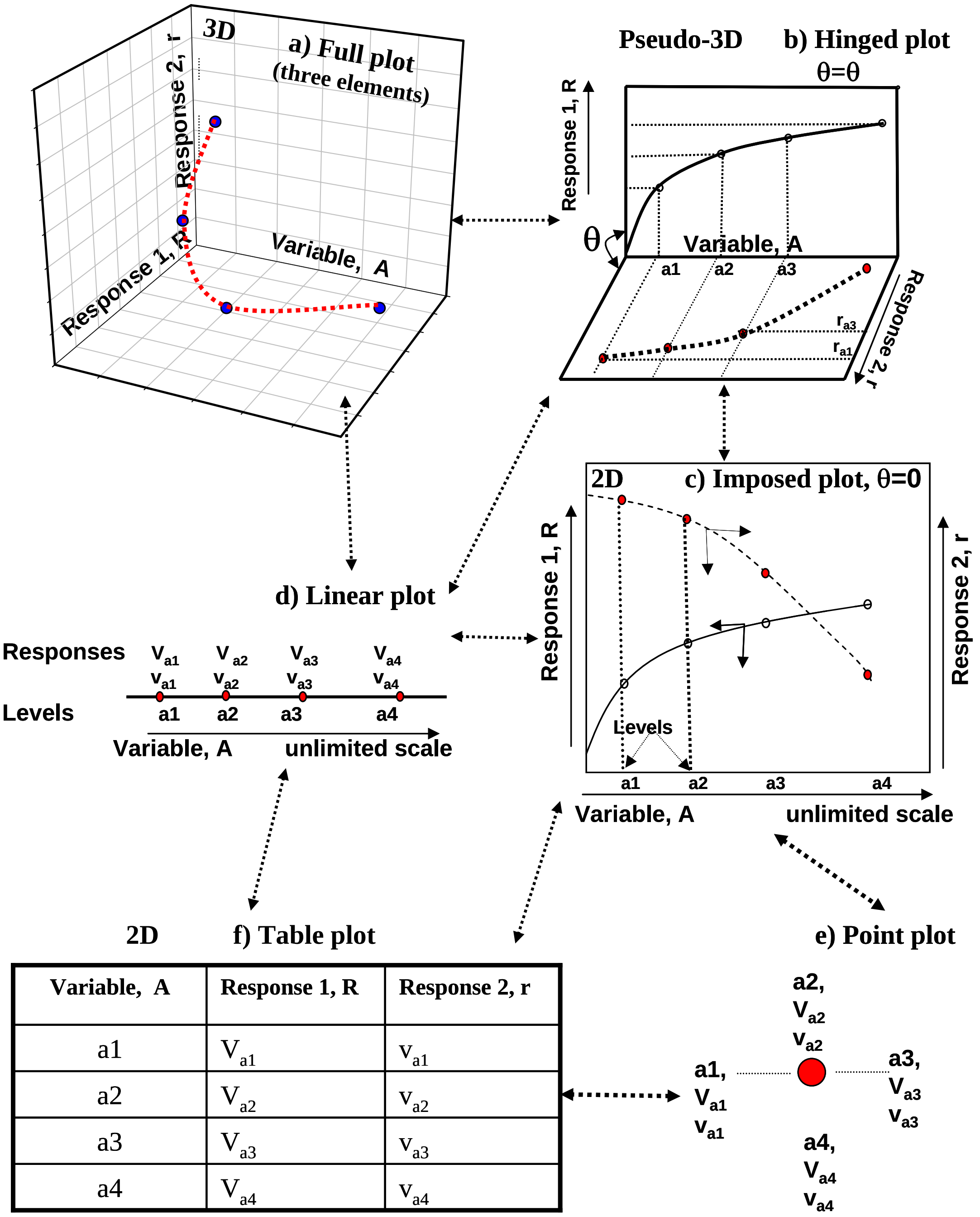


Fig. 22. Graphical representation of hypothetical flotation results for one variable and one response at different levels of the variable, a) 2D full plot, b) linear plot, c) point plot, and d) table plot

Sometimes there is a need to consider separation series affected by one variable (A) providing two responses (R and r) at each investigated level of the variable. In such a case, we have values of the two responses: V_{a1} and v_{a1} for the a1 level of variable A, V_{a2} and v_{a2} for the a2 level of variable, etc. A full plot for this case is a three-dimensional (3D) graph (Fig. 23a) on which each response is presented on a separate axis and the variable is shown on the third axis. The full plot (Fig. 23a) can be transformed to two 2D plots, that is one for each response (similar to Fig. 22a). It can also be separated into a pseudo-3D hinged plot with angle θ (Fig. 23b). When angle θ equals zero, the hinged plot (Fig. 23b) turns into a 2D imposed plot (Fig. 23c). It represents a superposition of two graphs from Fig. 22a. In this case, the variable level is read from the x-axis, while each response is read from the scales on the left and right sides of the y-axis. It is also possible to write the value of more than one flotation response at each variable level on the linear plot (Fig. 23d). Reading values from this plot will be confusing unless the two considered responses have a clear gap in their values. The plot becomes more complex when changing it into a point plot (Fig. 23e). Therefore, in this case the data table plot (Fig. 23f) seems to be more suitable.



Variable, A	Response 1, R	Response 2, r
a1	V_{a1}	v_{a1}
a2	V_{a2}	v_{a2}
a3	V_{a3}	v_{a3}
a4	V_{a4}	v_{a4}

Fig. 23. Graphical representation of hypothetical flotation results for one variable A and two responses (R and r) at different levels of the variable, a) 3D full plot, b) pseudo-3D hinged plot, c) 2D imposed plot, d) linear plot, e) point plot, and f) 2D table plot

3.3. Two variables

A separation system can be affected by two variables. Assuming that an interest is paid to only one response, the system now has three elements: variables A, B and response R. The full plot is thus a 3D graph (Fig. 24a) in which two axes accommodate the two variables, while the third axis represents the resulted response. In this plot, the plotted surface represents the response for all combinations of the two variables. There are different options to modify the full plot. Three of them are shown in Fig. 24. A projection of all responses on the two-variable base plane provides a 2D point-response plot (Fig. 24b). In this plot, the response points can be represented by $V_{a,b}$ where V is the value of response (R) at given levels of variables A and B, that is A=a and B=b. Thus, a and b can be read directly from the plot but the response value (V) must be indicated with a number. The response points $V_{a,b}$ in Fig. 24b can be connected in different manners providing different members in the family of response plots. One of them is the iso-response plot or contour map (Fig. 24c). Each line in the iso-response plot connects points having the same response value, that is for all “a,b” values located in one contour line the response value (V) = constant.

A second family of the reduced full plot is the response-level plot group. One of its members is shown in (Fig. 24d). It shows a 2D plot having one-axis for the response and the other accommodates one variable (A), while the second variable (B) is considered at constant levels (written in the plot). It can be generated by considering a group of lines crossing the contour map (Fig. 24c) parallel to the variable A axis. Thus, each line represents a constant level of variable B. For such a family of lines each point can be expressed by $R_{a,bx}$, where R is the response type. Its value can be read from the response axis while “bx” is the constant level of variable B (should be given) and “a” represents variable A level that can be read from the plot.

Another, third option, is the 2D response constant-level family of plots. It shows the response on one of the axes while the remaining axis is used for function “x” correlating both variables (A and B). Function “x” may be defined in different forms including x=A/B, B/A, A/(A+B), B/A+B, etc. Thus, its axis may have limited or unlimited scale. However, one of the variables is independent while the other becomes dependent. Figure 24e shows a member of the response constant-level family. It can be created from a group of lines crossing Fig. 24c parallel to the plot diagonal. Each line shows a constant total level of the two-variables, that is A and B.

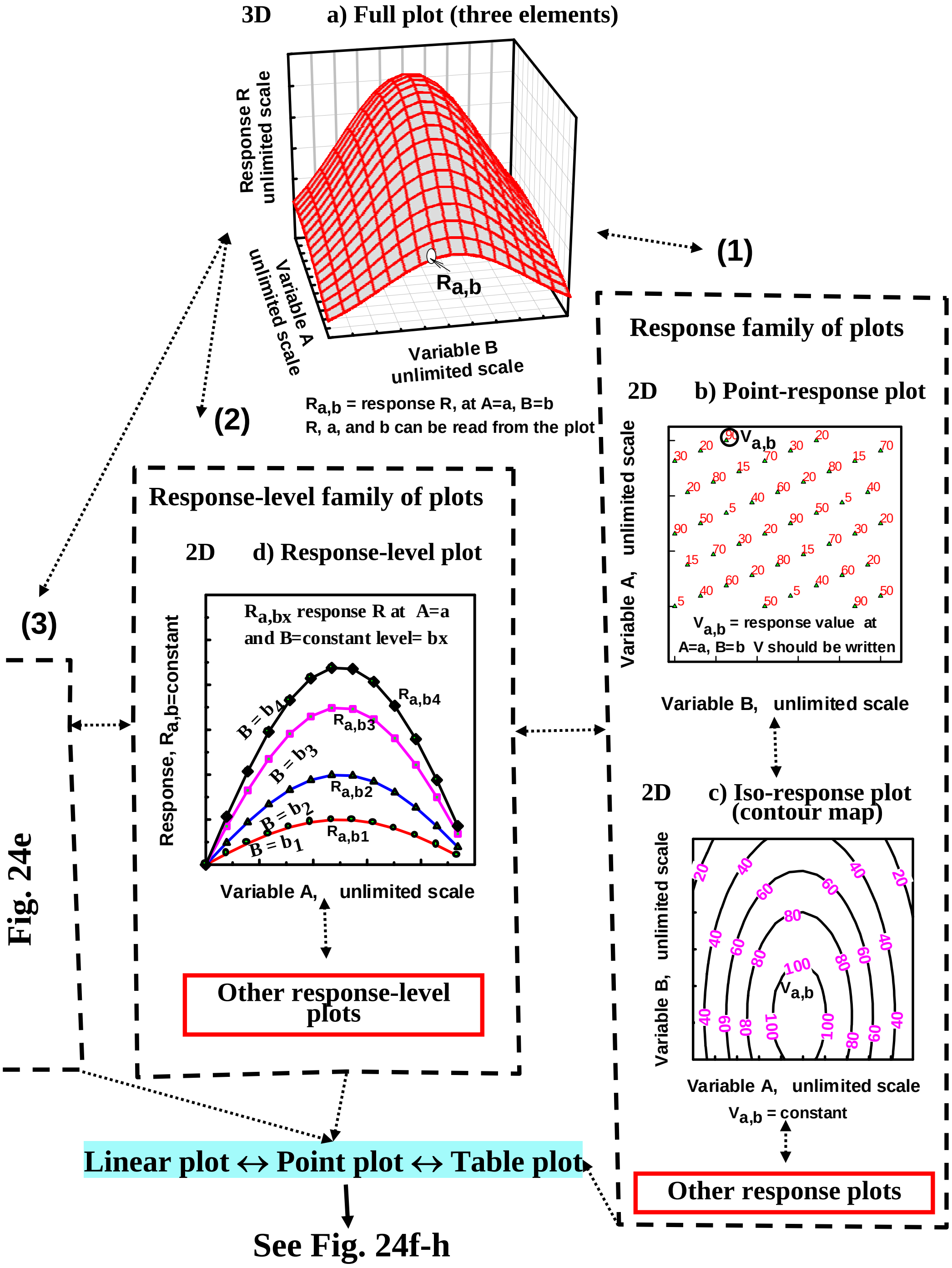
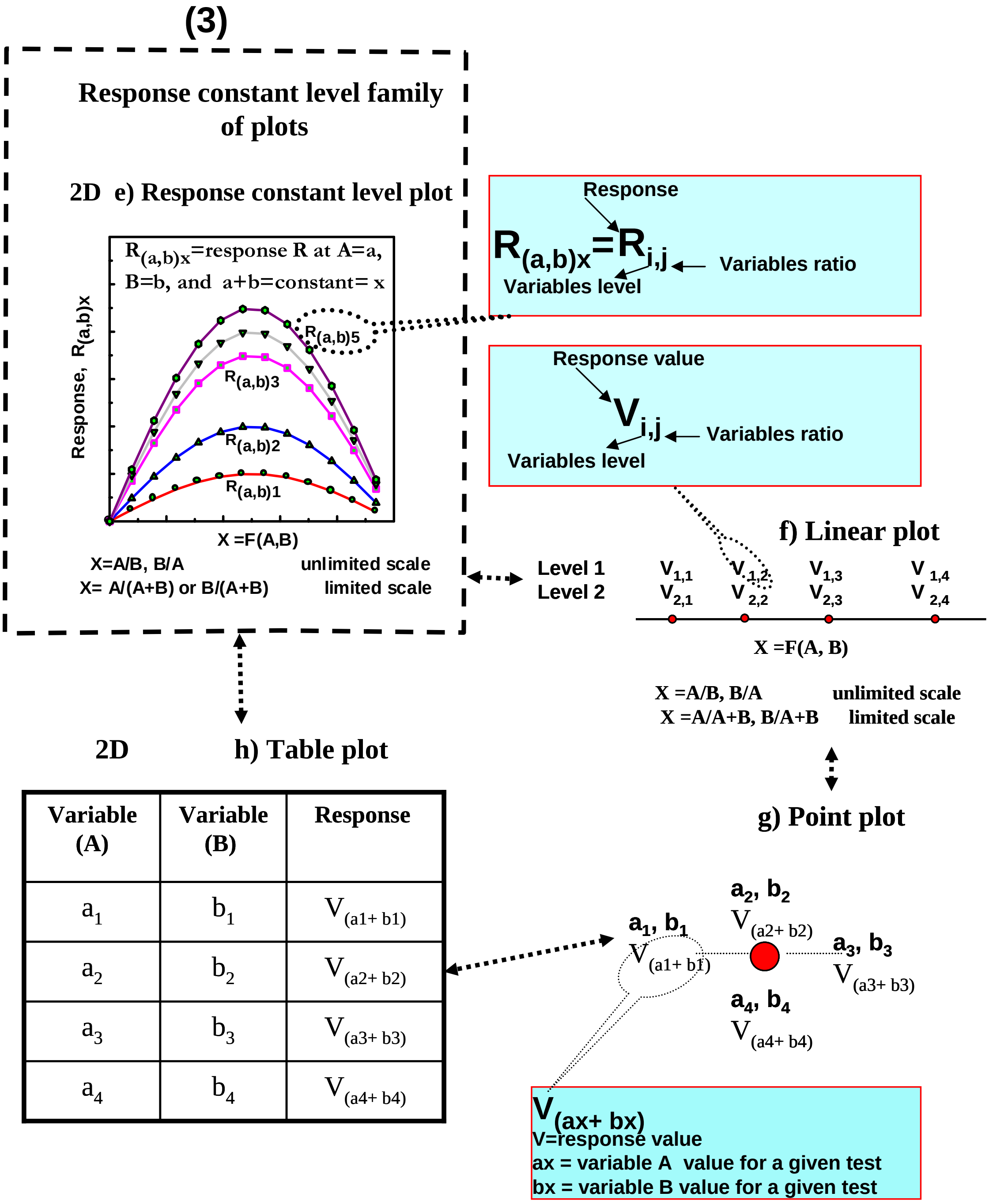


Fig. 24(a-d). Graphical representation of hypothetical flotation results affected with two variables providing one response, a) 3D full plot, b-c) 2D response family of plots, d) 2D response-level plots



Variable (A)	Variable (B)	Response
a_1	b_1	$V_{(a1+b1)}$
a_2	b_2	$V_{(a2+b2)}$
a_3	b_3	$V_{(a3+b3)}$
a_4	b_4	$V_{(a4+b4)}$

Fig. 24(e-h). Graphical representation of hypothetical flotation results affected with two variables providing one response, e) 2D response constant-level plot, f) linear plot, g) point plot, and h) 2D table plot

Each considered point can be expressed by $R_{(a:b)x}$, which means response at A:B=a:b at the total constant level of A+B=x. The full plot and its abbreviated forms can be transferred into a linear plot having the response values written at each considered combination of the two-variables (Fig. 24f). Figure 24f can be further abbreviated to a point plot (Fig. 24g) but reading from both of them is difficult, especially when two responses are to be considered. Therefore, it is recommended to convert the point plot to a table plot (Fig. 24h).

3.4. Three variables

When a separation process is affected by three variables (A, B, and C) and provides a response (R), then we deal with a four-element system. Its real full plot is a hypothetical one because it needs four axes. Such a hypothetical 4-axes graph can be converted to different response (3D) plots, some of which are given in Fig. 25(a-c). The reduced 3D forms depend on the variables interdependency. For instance, Figure 25a is a 3D plot having one of its axes accommodated for response R. Its second axis serves for independent variable (C), while the third axis is assigned for the other two-variables (A, B) assuming that they are related (one dependent and the other is independent). Therefore, this plot represents the case of two variables which are independent (A or B and C) and one is dependent (B or A). However, as the plot contains 4 elements or unknowns (A, B, C, and R), it should provide four sources of information to be completely readable. The axes represent three sources, and thus one more source is required. This source can be given by an equation to completely define the values extracted from the axis having two-variables. Meanwhile, if this axis have $x=A/B$, B/A, $A/(B+A)$ or $B/(B+A)$, then giving another information, for instance, $A+B=L1$, is necessary. Thus, with the four sources (3 axes + equation) all data can be extracted. It is worth mentioning that every $A+B=L$ value is called the level and thus, there is an unlimited number of levels. In the plot in Fig. 25a only two levels (1, and 2) are shown. More abbreviated forms of this plot will be further discussed in Fig. 26.

In the case when the three variables can be normalized, for example, by considering the dosage of three different reagents in a series of flotation tests, at different ratios between the three reagents, it is possible to plot the different considered combinations and the response in a 3D plot (Fig. 25b).

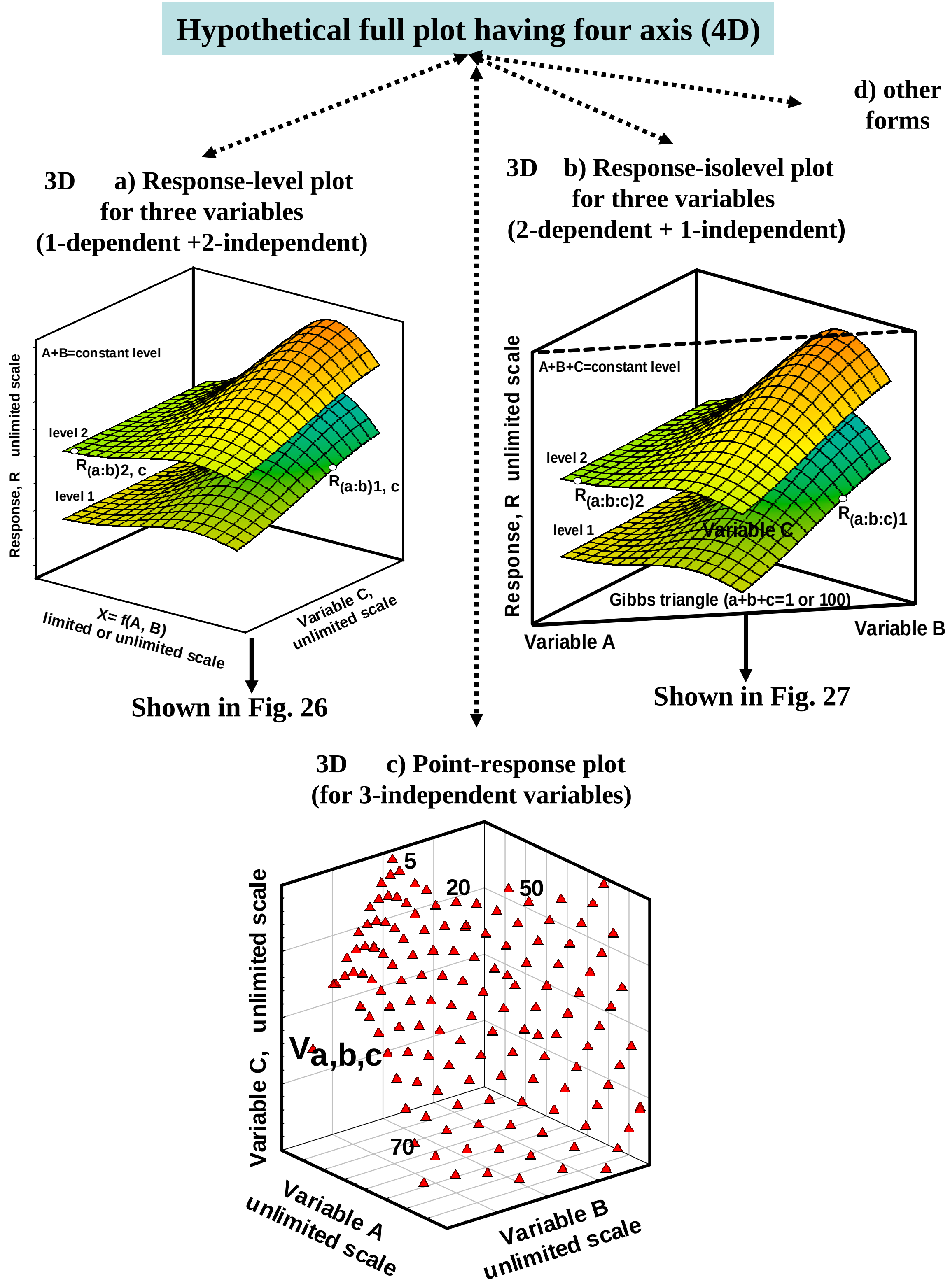


Fig. 25. Three-dimensional alternatives representing response plots for a 4-element system containing three variables and response, a) response-level plot for three variables (1-dependent+2-independent), b) response-isolevel plots for three variables (2-dependent+1-independent), and c) point-response plot for three independent variables

In this 3D plot (Fig. 25b), its 2D base is usually a triangle. The base triangle may be the well-known Gibbs triangle or a right-angle triangle. The apexes of the triangle represent the variables after normalizing their values for a known level, and thus only the ratios between variables can be read. The third axis of the plot represents the response. In the case of considering more than one level of the variables, each level can be drawn on a separate plot or all levels can be superimposed on the same graph having descriptors marking the different levels. This three-dimensional plot can be further abbreviated (Fig. 27).

Figure 25c represents a 3D plot having the three independent variables marked on its axes, and thus, the different studied combinations of the three variables are expressed as scattered points in the space. In this case, the corresponding response values must be written at each point while the values of the three variables can be read from the axes. It should be noted that any plane parallel to the two-variable plane represents a constant level of the third variable. At the same time, a constant level of the three variables can be expressed by a triangle. When there are many studied combinations and levels of the three variables, reading the response values from Fig. 25c becomes difficult and ambiguous. Therefore, it will be easier to draw in the space lines passing through points having the same response to create the 3D iso-response or contour map. In this 3D contour map, the contours show different nature than those drawn in the 2D contour map. They appear as if they were intersected but in fact they are not.

Figure 26a shows the first option of reducing the 4D hypothetical plot shown in Fig. 25a. It can be abbreviated to different families of lower dimension plots. The first family is the response family. It shows a 2D plot with one of its axes nominated for independent variable C, while the other serves for the other two variables (A, and B) provided that the total level value of the two variables together with the response value for each consider test are written (Fig. 26b). In the case the points having the same response value are connected, another member of the first family is generated. It is called the contour map or iso-response plot (Fig. 26c). In the contour map, each line parallel to the variable C axis represent a fix combination of variables A and B, while each line parallel to the A-B variables axes represents a constant level of variable C.

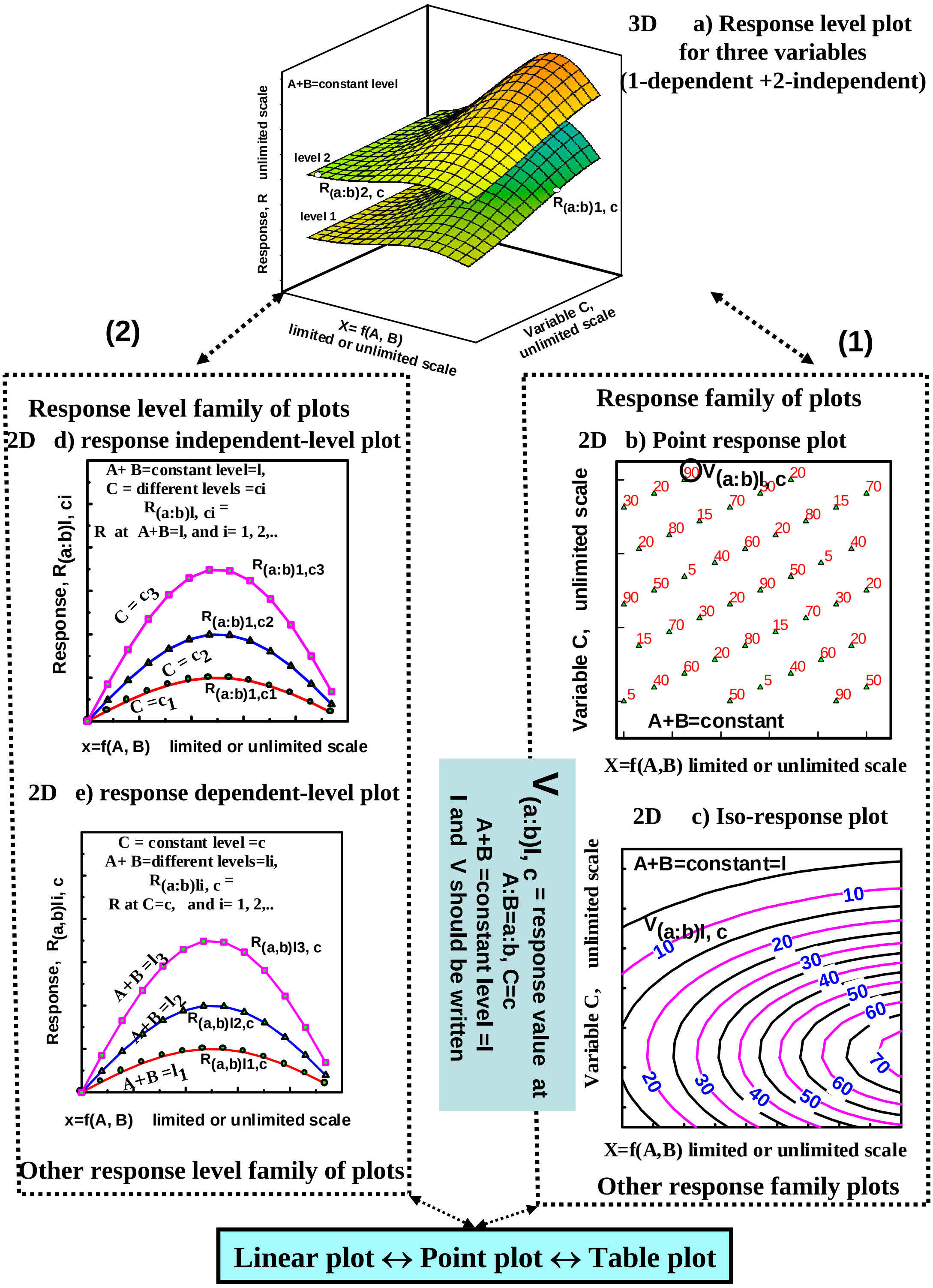


Fig. 26. Graphical representation of hypothetical flotation results affected with three variables and providing one response, a) 3D response plot, b) 2D point response map, c) 2D iso-response plot, d) 2D response independent level plot, e) 2D response dependent-level plot

At the same time, lines connecting a point located on the C axis with a point located on the A-B axis represent different combinations of the three variables at a total constant level of them. Therefore, another abbreviated family of Fig. 26a, called the response level family of plots, can be generated. Any member of this family can be created by considering a constant level of a variable or variables. For instance, Fig. 26d shows a response independent-level plot because the level of the two variables (A, and B) is constant for the whole series while the level of variable C is changing independently. On the other hand, the response dependent-level plot, given in Fig. 26e, shows different levels of variables A and B with a constant level of variable C. Further reduced forms of Fig. 26a are the linear, point and table plots, but they are not shown.

Figure 27a shows a second option of reducing the 4D hypothetical plot shown before in Fig. 25b. It can be also further abbreviated providing different families of lower dimension plots. The first family in this case is also the response family. The 2D point-response plot is a member of the first family. It may be done using the Gibbs triangle with written response values (Fig. 27b). The second member of the same family, called the iso-response plot, can be also created using the Gibbs triangle (Fig. 27c) or another right angle triangle (not shown). Fig. 27e presents a member of the response-level family of plots (Fig. 27a). It shows a right angle triangle having response on one axis and two variables at the other axis with plotted response lines showing different levels of the third variable C. In this case the total level of the three variables is constant. These two dimensional plots can also be reduced to linear, point, or table plots but will be very crowded. Therefore, they are not shown.

Three variables with more than one response can be treated for each response separately. Then, it reduces to the case shown in the previous section. Otherwise the analysis becomes more complex.

The hitherto considered cases are satisfactory for the needs of this thesis because systems considered in this thesis contain no more than four elements (3 reagents + response). In such cases, we shall use both response and iso-response two-dimensional plots for graphical representation of flotation upgrading results. It should be mentioned that, when the number of elements (variables + responses) in a given system are greater than the mentioned cases (i.e. >5) it becomes difficult to use normal three dimensional plots. In such cases, mathematical transformations become necessary. They may include neural networks, compahgin maps, etc as tools for the reduction of the number of the required axes.

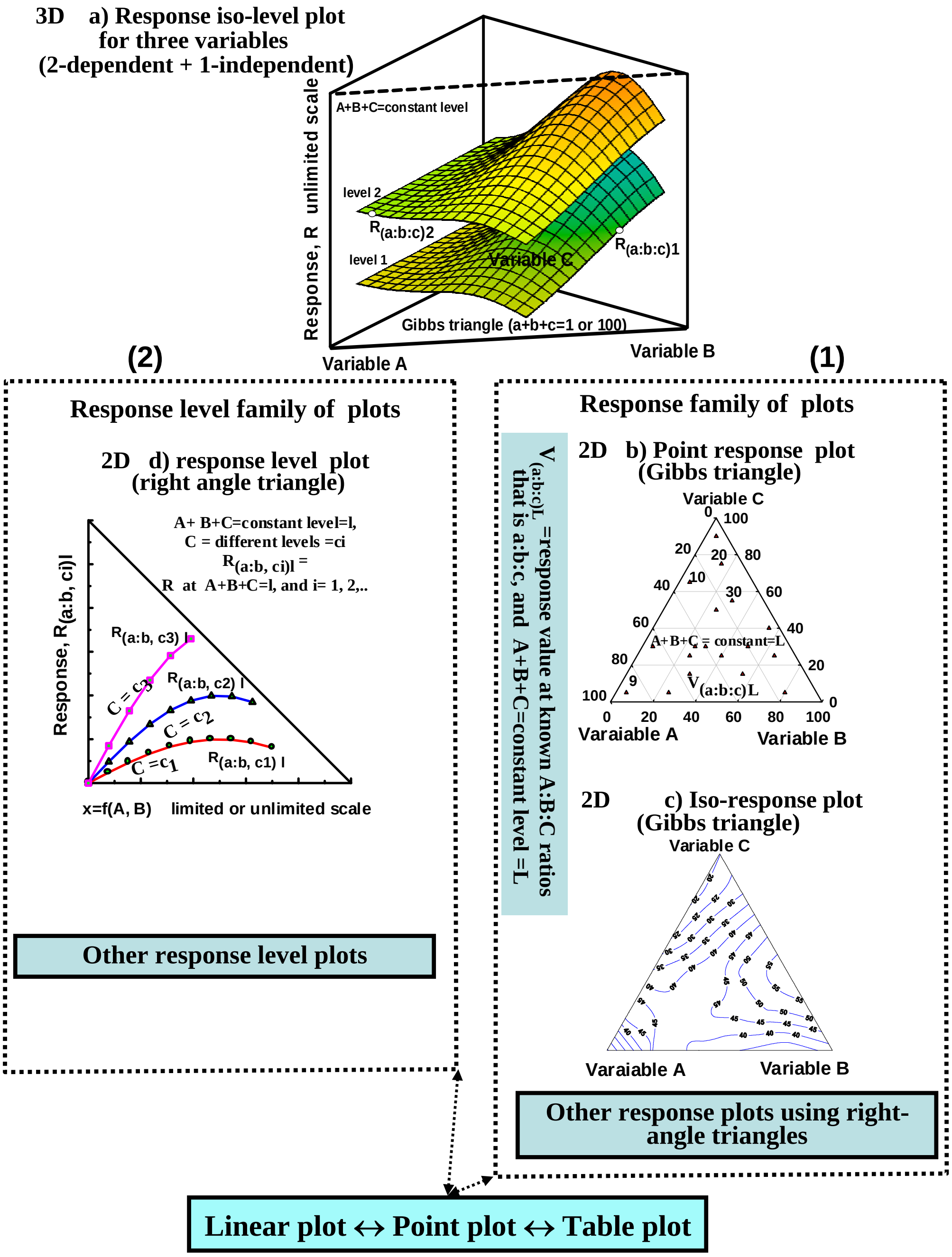


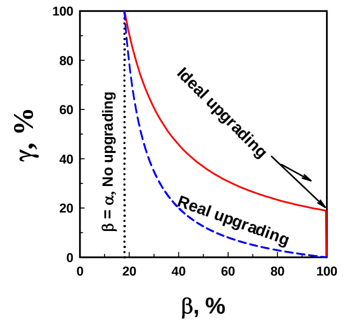
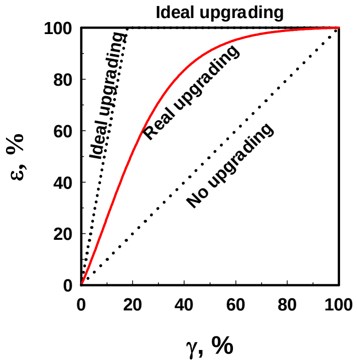
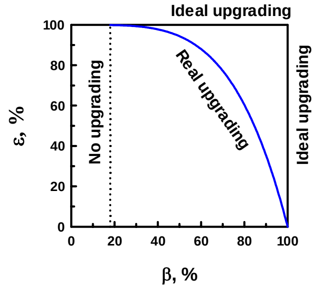
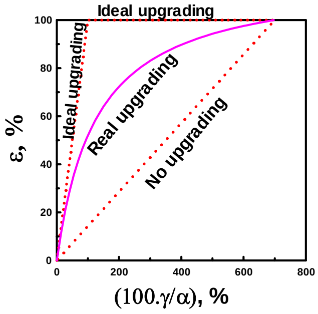
Fig. 27. Graphical representation of hypothetical flotation results affected with three-dependent variables and providing one response, a) 3D response plot, b) 2D point response plot (Gibbs triangle), c)2D iso-response plot (Gibbs triangle), d) 2D response level plot (right angle)

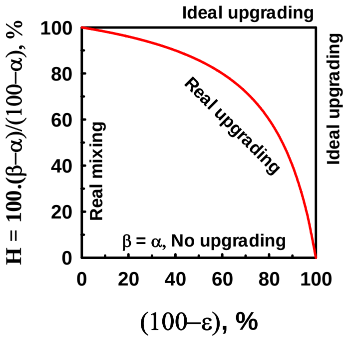
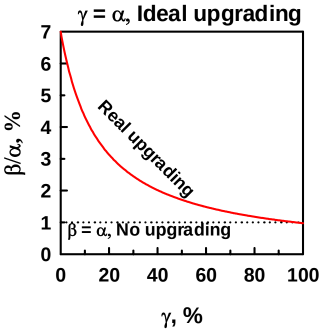
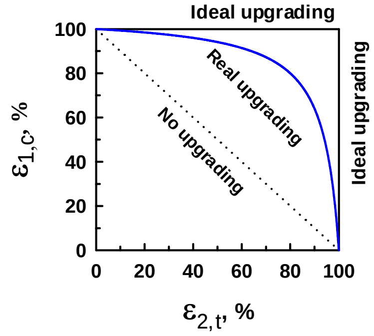
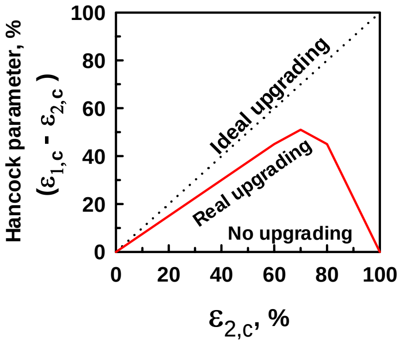
4. Evaluation and comparison of separation data using upgrading curves

4.1. Upgrading curves

After achieving flotational separation, it is important to judge, evaluate and/or compare the process results. According to Drzymala (2001b; 2005), very common evaluation of separation results is the upgrading approach. In this approach, a selected component of a separation system is considered as well as its quantity (mass or content in products) and the quantity of the products. If other parameters (feed quality, fluctuations, etc.) change during the separation, they also should be taken into account (Drzymala, 2005). For a system having a constant feed quality and being free of fluctuations (α=constant, F=0), the parameters that can be used for the evaluation of separation treated as upgrading are the yield of products (γ) and the contents of components in products (β) as well as in the feed (α=constant). Drzymala also (2003) showed that combinations of these two simple separation parameters and the feed content α provide infinitive number of new parameters called factors, numbers, coefficients, indices, ratios, efficiencies, etc. He was able to generate a family of such upgrading parameters using a general formula of $\gamma^a\ \beta^b\ \alpha^c$ where a, b, and c are constants equal to 0, ±1, ±2... ±n. This formula provides recovery ($\varepsilon=\gamma\beta/\alpha$; a=1, b=1 and c=-1), enrichment ratio ($k=\beta/\alpha$; a=0, b=1 and c=-1), Dell's parameter (γ/α; a=1, b=0 and c=-1 (Dell, 1953)), etc. Another family can be generated by subtracting upgrading parameters (Drzymala, 2003). For instance the Hancock parameter (Barskij and Rubinstein, 1970), having different mathematical forms, one of which is the recovery of one component in a certain product minus recovery of another component in the same product or shortly ($\varepsilon_{1,c}$-$\varepsilon_{2,c}$). The upgrading parameters can be tabulated and/or graphically plotted. Plotting two upgrading parameters against each other, result in what is called upgrading curves. Since there are unlimited numbers of upgrading parameters, the numbers of upgrading curves can also be infinitive (Drzymala, 2001b). It should be mentioned that all upgrading curves contain the same information concerning a separation process. The preference of one upgrading curve over the other depends on the nature of the considered feed and its resulted products as well as the aim of the separation process. Selected upgrading curves and their graphical forms are shown in Table 6.

Table 6. Selected upgrading curves used for graphical plotting and comparison of separation results. The case of α= constant, no fluctuations, and component = mineral

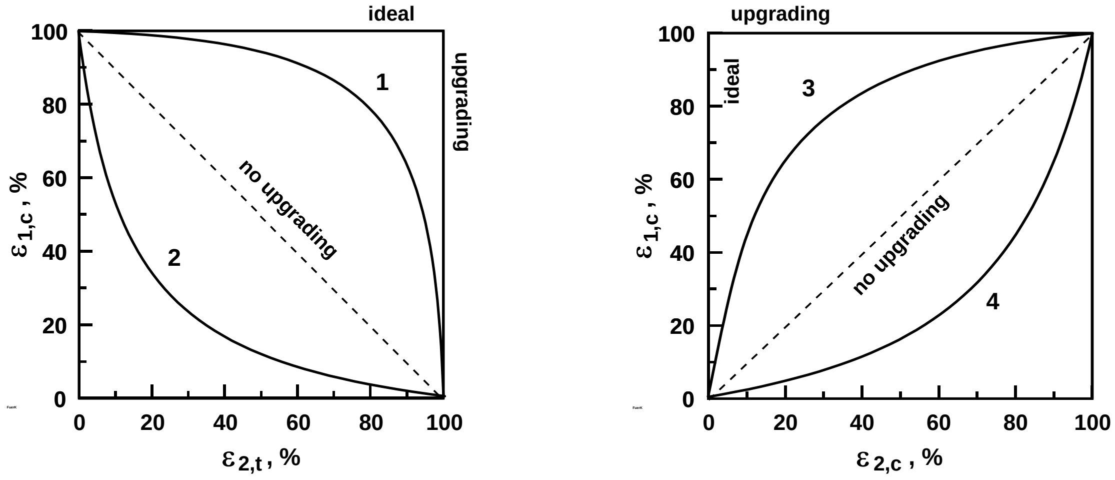
parameters	Plot shape	Reference
Product yield (γ) versus cumulative component content in this product (β). Feed content of the considered component is (α)	 Henry's plot	Henry, 1905; Reinhardt, 1911
Cumulative recovery of component in a certain product (ε) vs. product yield (γ)	 Mayer's plot	Mayer, 1950
Cumulative recovery (ε) of a certain component in a given product versus its cumulative content (β) in the same product	 Halbich's plot	Halbich, 1934
ε vs (100*γ/α) Where ε = cumulative recovery of component in a product, γ = the considered product yield, and α = content of the same component in feed	 Dell's plot	Dell, 1953; 1969; 1972

Hall's parameter $(100(\beta-\alpha)/(100-\alpha))$ vs recovery of component in other product $(100-\varepsilon)$	 Hall's plot	Hall, 1971
Component content in a certain product/its content in feed (β/α) versus the product yield (γ)	 Drzymala's plot	Drzymala, 2001b
Recovery of component 1 in concentrate $(\varepsilon_{1,c})$ Vs. recovery $(\varepsilon_{2,t})$ of second component in tailing	 Fuerstenau's plot	Fuerstenau, 1979; Harris et al., 1995; Sotillo et al., 1997; Jia et al., 2002; Drzymala, 2005; Drzymala and Ahmed, 2005
Hancock's parameter that is (recovery of component 1 – recovery of component 2) vs recovery of component 2 All should be in the same product	 Łuszczkiewicz's plot*	Łuszczkiewicz, 2002; Potulska, 2005

* Ideal and no upgrading lines were added by the author of this thesis

4.2. Fuerstenau's upgrading curves

One of the upgrading curves shown in Table 6 is Fuerstenau's plot relating recoveries of components in products of separation. The curve has two modifications (Figs. 28a and 28b).



a b

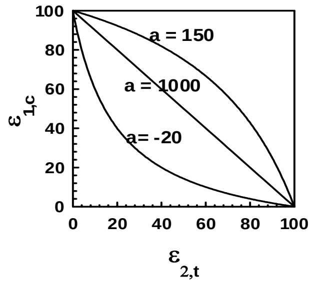
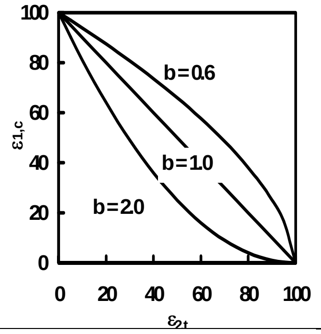
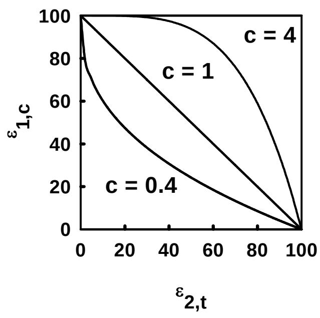
Fig. 28. The Fuerstenau upgrading curves: a) relationship between recovery of a component 1 in concentrate $\varepsilon_{1,c}$ and recovery of a second component in the tailing $\varepsilon_{2,t}$: 1 - recovery of component 1 in concentrate is greater than recovery of component 2 in concentrate, 2 - recovery of component 2 in concentrate is greater than recovery of component 1 in concentrate, b) relationship $\varepsilon_{1,c}$ vs $\varepsilon_{2,c}$: 3 - recovery of component 1 in concentrate is greater than recovery of component 2 also in concentrate, 4 - recovery of component 1 is smaller than recovery of component 2 in the same concentrate (after Drzymala and Ahmed, 2005)

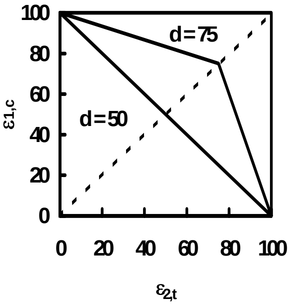
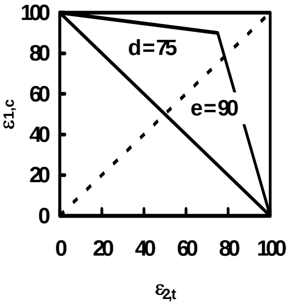
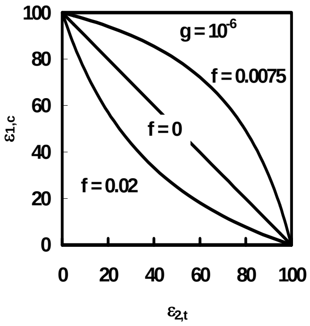
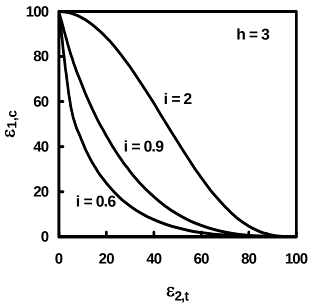
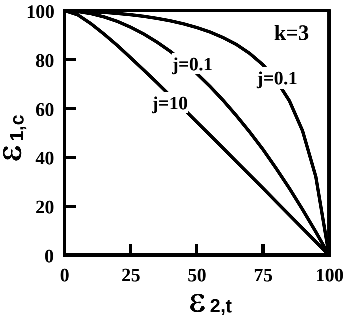
The Fuerstenau upgrading curves are very useful for evaluation of coal upgrading and have been extensively used by Fuerstenau and his co-workers (Fuerstenau, 1979; Harris et al., 1995; Sotillo et al., 1997; Jia et al., 2002). Therefore, Drzymala et al. (2003) proposed to call them the Fuerstenau upgrading curves. They will be used for evaluation of separation results in this thesis.

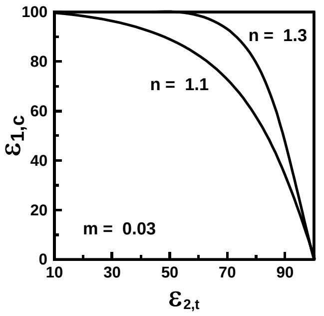
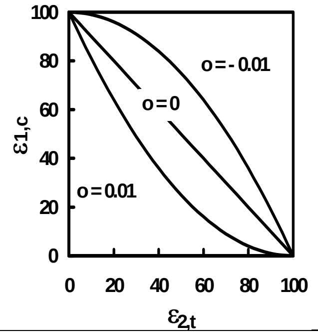
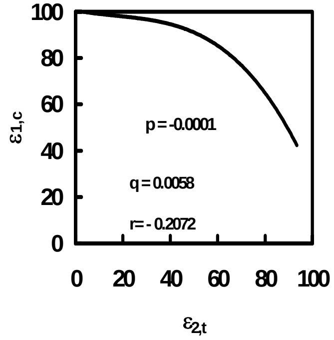
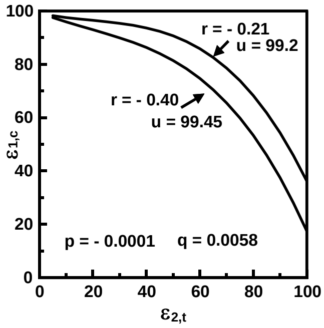
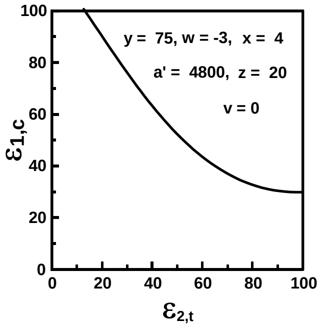
4.3. Mathematical formulas representing separation results plotted on Fuerstenau's upgrading curves

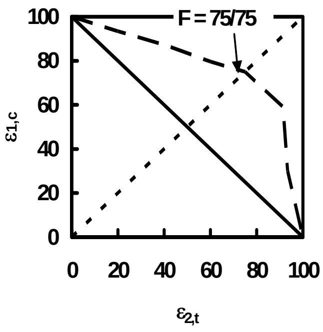
The upgrading curves are used for characterization, analysis and comparing of separation process. Sometimes, especially when the data points are scattered, the comparison of results of separation become more complex. Therefore, one of the options is statistical evaluation of the data with appropriate mathematical formulas. Due to Drzymala and Ahmed (2005) various equations are available for Fuerstenau's upgrading curves. Their formulas are of different characters (linear, polynomial, hyperbolic, exponential etc.,) and can contain different, from one to many, adjustable constants. A list of their equations and typical shapes of the curves generated with each equation are given in Table 7.

Table 7. Mathematical formulas, which can be used for approximation and statistical analysis of results plotted using Fuerstenau's upgrading curves (Drzymala and Ahmed, 2005)

Formula , curve shape, constant parameter	remarks	plot shape
One-adjustable parameter formula, fixed staring and ending points		
1 $\varepsilon_{1,c}$= a (100-$\varepsilon_{2,t}$)/(a-$\varepsilon_{2,t}$) (modified hyperbolic symmetrical) (Laplante et al., 1989) a	0<a<100 equation not defined -∞≤a≤0 upgrading in tailing 100≤ a ≤+∞ (upgrading in concentrate) a=100, 0 ideal upgrading a = ± ∞ no upgrading	
2 $\varepsilon_{1,c}$ = $(100-\varepsilon_{2,t})^b/100^{(b-1)}$ (exponential asymmetrical) b	b≥0 0≤b≤1 upgrading in concentrate 1≤b≤∞ upgrading in tailing b=1 no upgrading b=0, ∞ ideal upgrading	
3 $\varepsilon_{1,c}$= $(100^c-(\varepsilon_{2,t})^c)/100^{(c-1)}$ (exponential asymmetrical) c	c≥0 0≤c≤1 upgrading in tailing 1≤c≤∞ upgrading in concentrate c = 1 no upgrading c= 0, ∞ ideal upgrading	

<table>
<tr><td>4
$\varepsilon_{1,c}=100-\varepsilon_{2,t}(d-100)/d$
(upper half of straight line)
$\varepsilon_{1,c}=(\varepsilon_{2,t}-100)d/(d-100)$
(lower half of straight line), d</td><td>$0<d\leq 100$
$0<d\leq 50$ upgrading in tailing
$50\leq d\leq 100$ upgrading in concentrate
d=50 no separation
d=0, 100 ideal separation</td><td> </td></tr>
<tr><td colspan="3">Two-adjustable parameter formulas, fixed staring and ending points</td></tr>
<tr><td>5
$\varepsilon_{1,c}=100-\varepsilon_{2,t}(d-100)/d$
(Upper half of straight line)
$\varepsilon_{1,c}=(\varepsilon_{2,t}-100)e/(e-100)$
(lower half of straight line)
d, e</td><td>$0<d\leq 100$, $0<d\leq 50$ upgrading in tailing, $50\leq d\leq 100$ upgrading in concentrate, d=50 no separation, d=0 or 100 ideal separation, $0<e\leq 100$, $0<e\leq 50$ upgrading in tailing, $50\leq e\leq 100$ upgrading in concentrate, e=50 no separation, e=0, 100 ideal separation</td><td> </td></tr>
<tr><td>6
$\varepsilon_{1,c}=(100-\varepsilon_{2,t})/(1+f\varepsilon_{2,t}+g(\varepsilon_{2,t})^2)$
(fractional)
f, g</td><td>$g\neq 0$
range of f depends on value of g,
very small g gives good representation</td><td> </td></tr>
<tr><td>7
$\varepsilon_{1,c}=(100^i-(\varepsilon_{2,t})^i)^h/100^{(hi-1)}$
(exponential asymmetrical)
h, i</td><td>$h\geq 0$
$i\geq 0$
range of i depends on the value of h
no and ideal upgrading depend on the values of the two parameters.
i=1 (Eq. 7 = Eq. 2)
h=1 (Eq. 7 = Eq. 3)</td><td> </td></tr>
<tr><td>8
$\varepsilon_{1,c}=(j\varepsilon_{2,t}+k+100)(100-\varepsilon_{2,t})/(j\varepsilon_{2,t}+k+100-\varepsilon_{2,t})$
(fractional symmetrical), j, k</td><td>k = any value, j > 0
k values for no and ideal upgrading depend on j values
The equation given for upgrading in concentrate</td><td> </td></tr>
</table>

9 $\varepsilon_{1,c} = 100\left(1 - e^{-m(100-\varepsilon_{2,t})^{n}}\right)$ (Exponential asymmetrical) (Mohanty et al., 1999) m, n	$m > 0$, $n > 0$ m values for no and ideal upgrading depend on n values	
One- or more-adjustable parameter formulas, one fixed (starting or ending) point		
10 $\varepsilon_{1,c}=100-(1+100o)\,\varepsilon_{2,t} + o(\varepsilon_{2,t})^2$ (polynomial asymmetrical) o	for –0.01<o<0.01 fixed staring and ending points, o=0 no upgrading	
11 $\varepsilon_{1,c}= \ldots\ldots p(\varepsilon_{2,t})^3+ q(\varepsilon_{2,t})^2 + r\varepsilon_{2,t} + 100$ (polynomial) p, q, r	p, q, r can be any values	
one- or more-adjustable parameter formulas, no fixed starting and ending points		
12 polynomial equation $\varepsilon_{1,c}= \ldots\ldots p(\varepsilon_{2,t})^3+ q(\varepsilon_{2,t})^2 + r\varepsilon_{2,t} + u$ p, q, r, u	p, q, r can be any values u close to 100	
13 hyperbolic (sec. order eq. of a conic section) $v(100-\varepsilon_{2,t})^2 + 2w\,\varepsilon_{1,c}(100-\varepsilon_{2,t}) + x(\varepsilon_{1,c})^2 + 2y(100-\varepsilon_{2,t}) + 2z\varepsilon_{1,c} + a' = 0$ v, w, x, y, z, a’	v, w, x, y, z and a’ can be any values no and ideal upgrading can never be achieved	
characteristic point		

14 F=A;A or F=A/A $F=\varepsilon_{1,c}=\varepsilon_{2,t}$; $\varepsilon_{2,t}=\varepsilon_{1,c}$ (Fuerstenau et al., 1992) A	50<A<100 upgrading in concentrate 0<A<50 upgrading in tailing	

4.4. Evaluation of separation results obtained in this work

In this thesis, the Fuerstenau upgrading curve was utilized to judge the extent of separation because the recovery-rejection plot seems to be the most useful for this purpose. An approximation of the separation data can be accomplished with any of the equations shown in Table 7. It is generally known that when two or more separation formulas provide similar approximation, the one-adjustable parameter formula should be preferred over others. Therefore in this thesis, the most universal one-parameter equations (Eq. 1, Eq. 2, and Eq. 3, from Table 7), were tested for approximation of the coal upgrading curves using the Fuerstenau plot. A statistical evaluation of the one-parameter equations showed that Eqs. 1 and 2 from Table 7 were the best equations representing the separation data in this work. However, they were used in modified forms. In the case of Eq. 1 from Table 7 to have its selectivity parameter “a” assuming the values from 0 to 1, it was modified to:

$$\varepsilon_{c,1} = \mathbf{(100/A)(100-\varepsilon_{a,2})/((100/A)-\varepsilon_{a,2})} \qquad (1B)$$

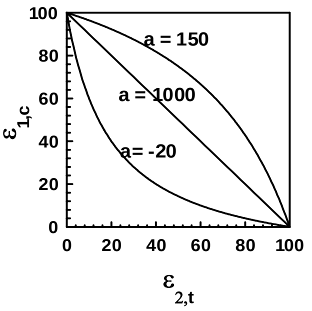
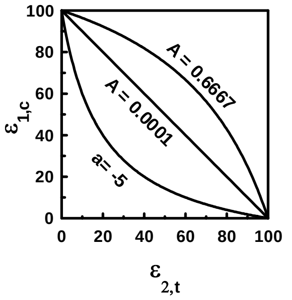
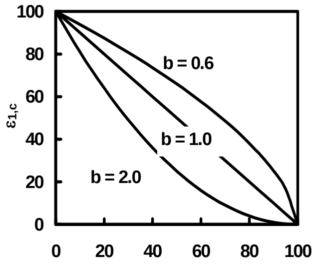
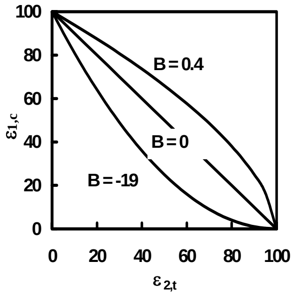
In the case of Eq. 2 from Table 7, to have its constant "b" equal to "0" for lack of upgrading and "1" for ideal upgrading, this equation was modified to:

$$\varepsilon_{c,1} = \mathbf{(100-\varepsilon_{a,2})^{(1-B)}/100^{(-B)}} \qquad (2B)$$

where

$\varepsilon_{c,1}$ and $\varepsilon_{a,2}$ recoveries defined in Fig. 28, **A** = adjustable constant or selectivity parameter having values from 0 to 1 (Eq. 1B). **B** = adjustable constant “called selectivity parameter" also having values from 0 to 1 (Eq. 2B). The boundary conditions and the plot shapes of both original and modified forms of the two equations are given in Table 8.

Table 8. One-parameter equations used for approximation and statistical analysis of results obtained in this thesis using Fuerstenau's upgrading curves

Formula , curve shape, constant parameter	remarks	plot shape
Eq. 1A $\varepsilon_{c,1}=$ $a\,(100-\varepsilon_{a,2})/(a-\varepsilon_{a,2})$ (modified hyperbolic symmetrical) (Laplante et al., 1989) **a**	$0<a<100$ equation not defined $-\infty\le a\le 0$ upgrading in tailing $100\le a\le+\infty$ (upgrading in concentrate) a=100, 0 ideal upgrading $a=\pm\infty$ no upgrading	
Eq. 1B $\varepsilon_{c,1}=$ $(100/A)(100-\varepsilon_{a,2})[(100/A)-\varepsilon_{a,2}]^{-1}$ (fractional symmetrical) A	$\infty\ge A\ge 1$ equation not defined $-\infty\le A<0$ upgrading in tailing $0<A<1$ (upgrading in concentrate) A=1, -∞ ideal upgrading A = 0, no upgrading	
Eq. 2A $\varepsilon_{c,1}=$ $(100-\varepsilon_{a,2})^{b}/100^{(b-1)}$ (exponential asymmetrical) b	$b\ge 0$ $0\le b\le 1$ upgrading in concentrate $1\le b\le\infty$ upgrading in tailing b=1 no upgrading b=0, ∞ ideal upgrading	
Eq. 2B $\varepsilon_{c,1}=$ $(100-\varepsilon_{a,2})^{(1-B)}/100^{(-B)}$ (exponential asymmetrical) B	$B\le 1$ $0\le B\le 1$ upgrading in concentrate $-\infty\le B\le 0$ upgrading in tailing B=1 ideal upgrading in concentrate B=0 no upgrading B= -∞ ideal upgrading in tailing	

This is in line with Drzymala's (2005) claim that for a two (or more) products, two (or more) components separation system, where two parameters (quality and quantity) vary in the separation, the minimum required number of either parameters, elements, or parameters and elements for characterizing the separation process is two. In my case the two parameters will be changed to one element and a parameter:

1- equation used, (element)

2- equation adjustable constant, (parameter).

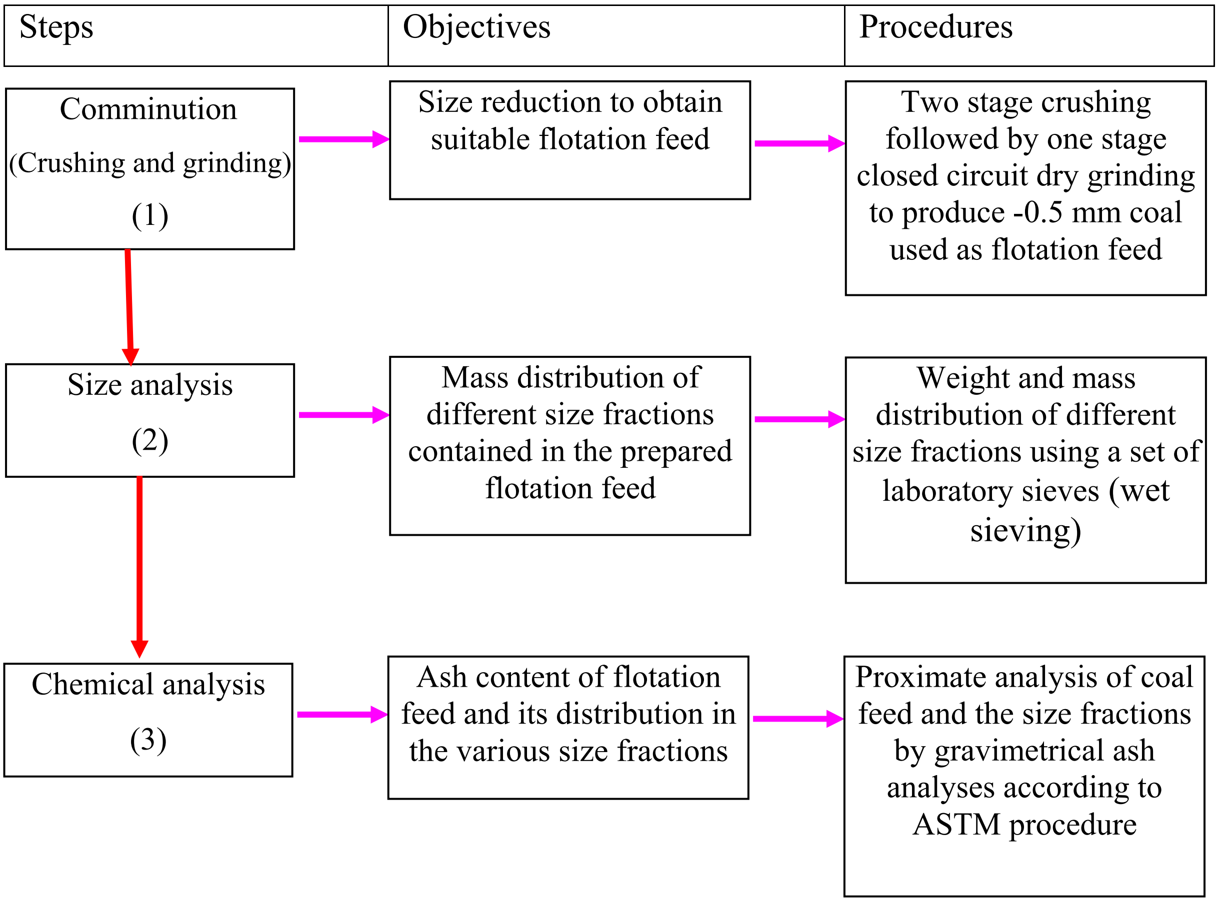
Therefore, a comparison of separation data for the same component using the same equation for approximation of the results can be accomplished by comparison of the adjustable constant A (or B). If the data are scattered, it means another variable was operating in the system and thus another parameter or element is needed for evaluation of results. The most suitable is a carefully selected statistical parameter which can also indicate the degree of approximation of separation results with the equation used. This approach allows comparing the result of coal cleaning studied in this thesis using only one parameter and the selected equation for approximation of the data for the same component (here either ash or carbonaceous matter).

INVESTIGATORY PART

5. Materials and methods

5.1. Coal preparation and its characterization

About 100 kg of run-of-mine coal sample from the Kazimierz Juliusz mine, located in Sosnowiec (Poland), was used. The preparation and characterization of coal together with objectives and procedures are summarized in Fig. 29.



Steps	Objectives	Procedures
Comminution (Crushing and grinding) (1)	Size reduction to obtain suitable flotation feed	Two stage crushing followed by one stage closed circuit dry grinding to produce -0.5 mm coal used as flotation feed
Size analysis (2)	Mass distribution of different size fractions contained in the prepared flotation feed	Weight and mass distribution of different size fractions using a set of laboratory sieves (wet sieving)
Chemical analysis (3)	Ash content of flotation feed and its distribution in the various size fractions	Proximate analysis of coal feed and the size fractions by gravimetrical ash analyses according to ASTM procedure

Fig. 29. Sequence of preparation and characterization of the investigated coal sample

The first step (comminution) was accomplished by two-stage primary crushing of the 100 kg coal sample in a “Denver” jaw crusher to less than 5-cm product. The primary crushed sample was thoroughly mixed, and quartered, and about 50 kg of the representative sample was dry-ground using a hammer mill running in a closed circuit with a 0.5 mm screen to produce –0.5 mm material. The next step (size analysis) was carried out for coal prepared as flotation feed using a set of laboratory sieves to determine the particle size distribution. The different obtained size fractions were filtered, dried, and weighted. A representative sample from each size fraction was kept for step 3.

The next activity (step 3) included chemical analysis of both the flotation feed and its different size fractions (obtained in step 2). It was achieved using a representative sample from the flotation feed (about 2 kg prepared by the Jones sampler) in addition to samples collected from the different size fractions. Each sample was successively ground using a porcelain abrasion mill until it was passing the 75-μm screen. The flotation feed sample then was subjected to a proximate chemical analysis including determination of moisture, ash and combustible matter contents, while the samples of the different size fractions were analyzed only for ash contents. The analyses were run according to the American Society for Testing and Materials ASTM (D4182-97).

The size distribution of flotation feed (obtained after steps 1 and 2) and its ash contents (obtained after step 3) are shown in Table 9.

Table 9. Size distribution and ash analysis of the flotation feed considered in this work

Fraction # (i)	Size fraction, $d_{i-1,\,i}$ mm	Size fraction content in the feed, γ_i, wt., %	Ash content in the size fraction, λ_i %
1	-0.075	39.85	4.50
2	-0.106+0.075	17.87	3.62
3	-0.150+0.106	12.78	2.52
4	-0.250+0.150	15.81	2.36
5	-0.500+0.250	13.69	1.56
Calculated feed		100.0	3.35
Actual feed		100.0	3.38

The cumulative size distribution of the feed is shown in Fig. 30, while the proximate chemical analyses of the coal sample is shown in Table 10.

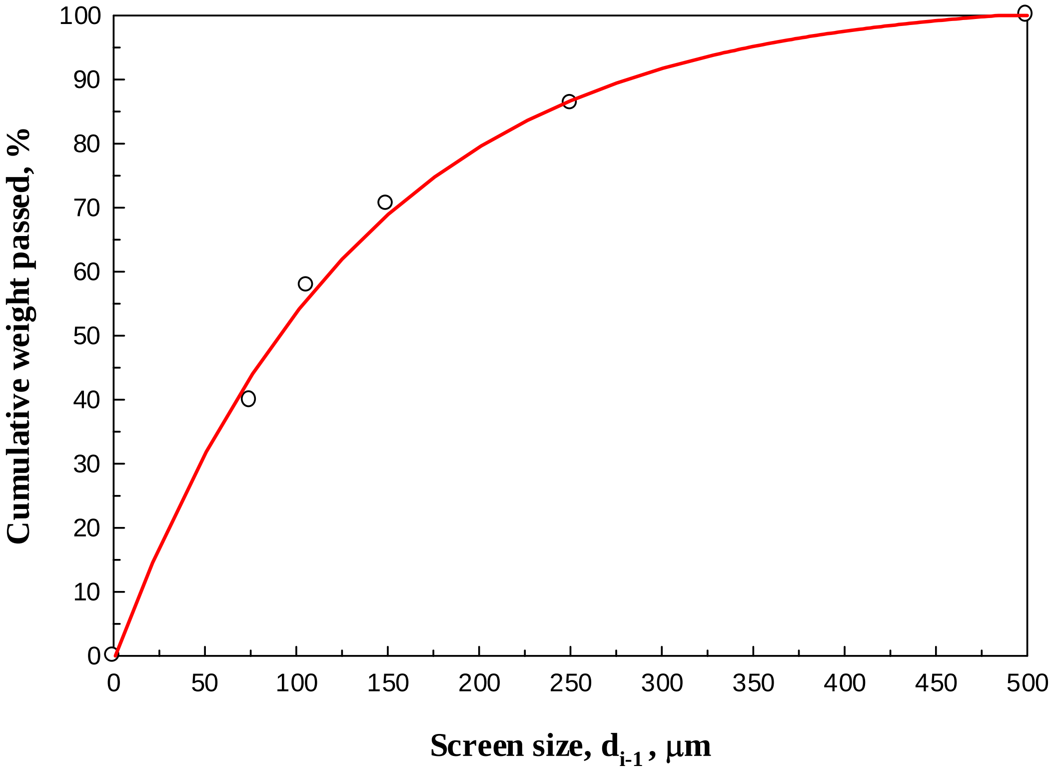


Fig. 30. Cumulative size distribution of the considered flotation feed

Table 10. Proximate chemical analyses of Kazimierz Juliusz Sosnowiec coal

Component	%
Moisture	10.80
Ash	3.38
Combustible matter (carbonaceous matter)	85.82
Loss on ignition (LOI) (moisture + combustible matter)	96.62

5.2. Reagents used

Three categories of chemicals were used. They were hydrocarbons (heptane and dodecane), alcohols (1-pentanol and α-terpineol), and alkyl poly(ethelene glycol) ethers (C_xE_y) such as hexadecyl tricosa(ethylene glycol) ether ($C_{16}E_{23}$), and dodecyl tetra(ethylene glycol) ether ($C_{12}E_4$). The properties provided by the manufacturer together with other properties of the reagents are listed in Table 11. They all were of commercial grades and were used without further purification.

Table 11. Properties of reagents considered for coal flotation studies in this thesis, at 25 °C

Reagent	Manufacturer	Molar mass (g/mol)	Phase	Solubility in water [a] g/dm^3	Density g/cm^3
Heptane (C_7H_{16})	Fluka	100.21	Liquid	0.002	0.726
Dodecane ($C_{12}H_{26}$)	Fluka	170.34	Colorless liquid (boils at 216 °C)	Insoluble	0.749
$C_{12}E_4$* ($C_{20}H_{42}O_5$)	Fluka	362.23	Viscous colorless liquid (viscosity 30 cP)	Insoluble with CMC ~ $4 \cdot 10^{-5}$ mole/dm^3 (Berthod et al., 2001)	1.109
$C_{16}E_{23}$** ($C_{62}H_{126}O_{24}$)	Fluka	1254	Solid	Insoluble with CMC ~ $2 \cdot 10^{-7}$ mole/dm^3 (Berthod et al., 2001)	1.157
1-pentanol ($C_5H_{12}O$)	Fluka	88.15	Colorless liquid (boils at 137.3 °C)	Moderately soluble (22.66)	0.811
α-terpineol ($C_{10}H_{18}O$)	Fluka	154.25	Liquid (normally solid if pure)	Low solubility (1.987)	0.948

a- data from the web unless mentioned (http://homepages.uc.edu:8000/~maynarjb/482/refer/propert.htm)

* dodecyl tetra(ethylene glycol) ether ** hexadecyl tricosa(ethylene glycol) ether

Double distilled water was used for preparation of the reagent stock. When the reagents formed emulsion, the ultrasonic energy was applied for a better dispersion. It was applied in intermittent short time intervals to avoid heating of the system.

5.3. Phase diagram of hydrocarbon-water-C_xE_y system

The dodecane-$C_{12}E_4$-water phase diagram at room temperature (25 °C) was created especially for this work. To distinguish different possible phases and their approximate boundaries, different concentrations, on weight percent basis, were considered (Fig. 31). At each concentration, an appropriate amount of dodecane was added (during a continuous magnetic stirring) to the necessary amount of $C_{12}E_4$ followed by the required amount of distilled water. The system was homogenized by further stirring for 0.5 min. To ensure good mixing, the sample was further stirred for additional 20 s using a Techpan UD-11 ultrasonic device. Next, the sample was observed visually for changes in turbidity, phase separation, or gel formation. Another similar sample was prepared for analyses with a UV spectrophotometer. In the case of physical changes, the expected emulsion or two-phase solution was claimed basing on similar literature systems. When the sample was transparent, it was tested periodically for at least 7 days for any changes. If the clarity has persisted, the system was considered either solution or microemulsion, depending on the water content. Figure 31 shows the experimental points which represent the investigated combinations of reagent concentrations.

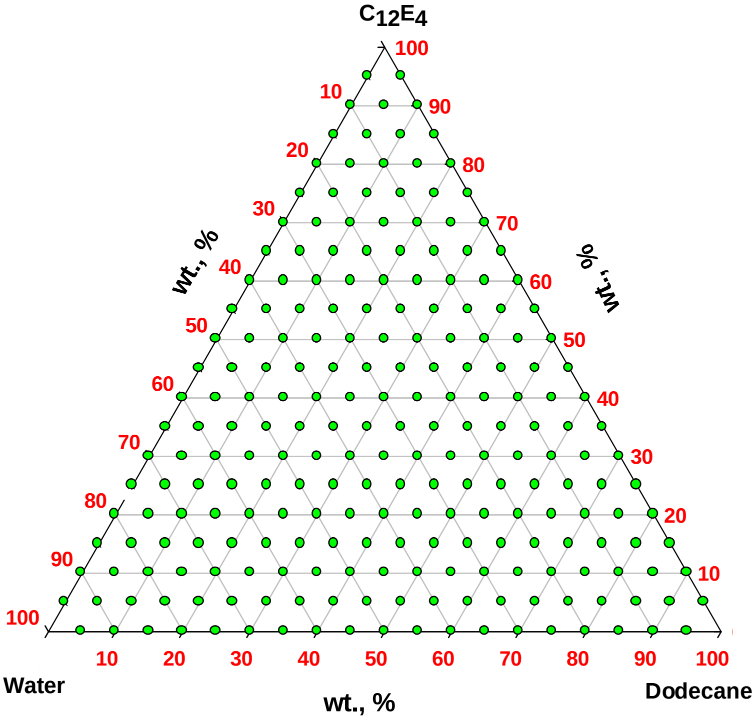


Fig. 30. Investigated concentrations to create phase diagram of the dodecane-$C_{12}E_4$-water system. Circles indicate considered concentrations

5.4. Flotation procedures

5.4.1. General information

Flotation tests were carried out in a Mechanobr mechanical sub-aeration laboratory flotation machine equipped with a 1-dm^3 net capacity cell. The cell total volume was 1.2 dm^3, while 0.2 dm^3 volume was devoted to the emerged parts of the flotation machine in the cell. Aeration rate and stirring speeds were constant throughout the work and were 0.0015 m^3/min and 1300 rpm, respectively. The pH of flotation was natural (6.1) and flotation time was always 10 min. In most experiments, this 10-minute concentrate collection time represented the infinite flotation time after which the froth was "empty". Both flotation products, that is the clean coal (concentrate) and residual (tailing), were filtered, dried at 100-105^{o}C, weighted, and analyzed for the ash contents. For accuracy purpose, the feed ash was calculated utilizing the concentrate and tailing ash contents and it was compared to the ash content of the original feed sample containing 3.8 % on moisture free bases. When the error was found within an acceptable range (less than 1%), the further calculations were based on the ash content for the calculated feed. When the error was greater, the whole experiment was canceled.

To find the best reagent and procedure regime of flotation of the investigated coal, different combinations were tried, which are described in the following sections.

5.4.2. Normal-contact flotation procedure (NCF)

The normal-contact flotation procedure relied on wetting or cleaning a 100 g of dry coal in tap water by conditioning for 3 min of the formed pulp containing ~65% solid/liquid ratio (by weight) (*wetting or cleaning stage*). It was followed by addition of the required dosage of reagent or reagents determined by reagent/s dosage and stock solution concentration (dissolved or dispersed in distilled water). When more than one reagent were used, each of them was added separately and the same conditioning time (3 min) was applied after each reagent addition. The reagents addition and conditioning stage can be called shortly *the adsorption stage*. Next, the system was diluted to 10% solid/liquid pulp by adding the required amount of tap water and stirring for 3 min. This stage can be called 10%-solid/liquid pulp agitation step or shortly the *10% stage*. Next, the system was aerated for initiation of the process (*flotation stage*). This procedure was applied in two versions. The one described above will be called the normal-contact flotation-version A or shortly NCF/A.

The other version, NCF/B, relies on adding reagents not one-by-one but as a mixture prepared in distilled water followed by a 3 min conditioning time after the wetting or cleaning stage (*adsorption stage*). Next, the system was diluted to 10%

solid/liquid by adding the required amount of tap water and stirred for 3 min (*10% stage*). Then, the system was aerated for initiation of the process (*flotation stage*).

For more clear presentation of the difference between the two versions of the normal-contact flotation, the (water+coal) + dodecane-$C_{12}E_4$ (that is a two-reagent system) is considered as an example in Table 12. It is assumed that a flotation test is to be run using 10 g/kg of the two reagents (5 g/kg each) and the reagent/s aqueous stocks are 1% by weight in distilled water.

Table 12. Steps of a hypothetical flotation test carried out applying both versions of normal-contact flotation procedure using 10 g/kg dodecane + $C_{12}E_4$ (5g/kg each)

Normal contact, (NCF/A)	**Normal contact, (NCF/B)**
1- coal (100 g) is stirred in tap water for three minutes at 65 % solid/liquid ratio → (*wetting or cleaning stage*)	1- coal (100 g) is stirred in tap water for three minutes at 65 % solid/liquid ratio → (*wetting or cleaning stage*)
2a- Addition of 50 cm^3 from 1% dodecane aqueous stock to represent the required dosage of dodecane (5g/kg) and further agitation for another three min pulp from step (1) + dodecane (5 g/kg)	2- addition of 100 cm^3 from 1% (dodecane-$C_{12}E_4$) aqueous stock (in which dodecane/$C_{12}E_4$ ratio equals 1) representing 10 g/kg from both reagents distributed according to their relative ratio in the stock. Agitation for three min after the single-step reagents addition. pulp from step (1) + 10g/kg of (dodecane + $C_{12}E_4$) → (*adsorption stage*)
2b- addition of 50 cm^3 from 1% $C_{12}E_4$ aqueous stock for 5 g/kg $C_{12}E_4$ dosage and agitation for three min pulp from step (2a) + $C_{12}E_4$ (5 g/kg)) → (*adsorption stage*)	
3- addition of necessary dilution tap water followed by three min conditioning (*10% stage*)	3- addition of necessary dilution tap water followed by three min conditioning (*10% stage*)
4- starting aeration and flotation (*flotation stage*)	4- starting aeration and flotation (*flotation stage*)

The reagent/s used in both versions of this procedure together with the investigated parameters are described in Table 13.

Table 13. Summary of reagents (stock solutions and investigated parameters) considered during NCF flotation procedure of coal

(NCF/A)

Number of reagents used	Reagent type	Reagent name	Reagent stock	Studied parameter
One reagent	Hydrocarbon	heptane	1% (by wt.) reagent in water (emulsion)	dosage of reagent
		dodecane		
	Alcohol	pentanol*	1% (by wt.) reagent in water (solution or emulsion)	dosage of reagent
		terpineol**		
	C_xE_y	$C_{12}E_4$	1% by wt. reagent in water (micellar solution)	dosage of reagent
		$C_{16}E_{23}$		
Two reagents	Hydrocarbon and alcohol	heptane-pentanol	each reagent stock was 1% (by wt.) in water	a) two reagent ratio at 4 g/kg, b) two reagent dosage at optimum ratio
		dodecane-pentanol		
		heptane-terpineol		
		dodecane-terpineol		
	Hydrocarbon and C_xE_y	heptane-$C_{12}E_4$	each reagent stock was 1% (by wt.) in water	a) two reagent ratio at 4 g/kg, b) two reagent dosage at optimum ratio
		dodecane-$C_{12}E_4$		
		heptane-$C_{16}E_{23}$		
		dodecane-$C_{16}E_{23}$		
	Alcohol and C_xE_y	$C_{12}E_4$-pentanol	each reagent stock was 1% by wt. reagent in water	a) two reagent ratio at 4 g/kg, b) two reagent dosage at optimum ratio
		$C_{12}E_4$-terpineol		
		$C_{16}E_{23}$-pentanol		
		$C_{16}E_{23}$-terpineol		
Three reagents	Hydrocarbon, C_xE_y and alcohol	dodecane, $C_{12}E_4$ and pentanol	each reagent stock was 1% by wt. in water	three reagent ratios at 4 and 10 g/kg

(NCF/B)

Number of reagents used	Reagent type	Reagent name	Reagent stock	Studied parameter
Two reagents	Hydrocarbon and C_xE_y	dodecane-$C_{12}E_4$	different dodecane-$C_{12}E_4$-water concentrations	two-reagent-water ratios at (dodecane+$C_{12}E_4$) dosage of 10 g/kg

* pentanol stands for 1-pentanol **terpineol refers to α-terpineol

5.4.3. Direct-contact flotation procedure (DCF)

In this procedure, the 100g dry coal sample was first mixed with either pure reagent(s) or a solution containing an appropriate amount of reagent/s (*reagent-coal contact stage or adsorption stage*). This step was designed to create environment for either direct contact of anhydrous reagents with coal or direct contact of different forms of reagents present in the considered solutions (surfactant solutions, emulsions, microemulsions) added in one portion. In the case of using anhydrous reagents (added one-by-one) the procedure is called "direct-contact flotation version A" or shortly DCF/A. When aqueous reagents were contacted with coal directly, the procedure will be referred to as the "direct-contact flotation version B" or shortly DCF/B. After the coal-reagent contact or adsorption stage, both procedures followed the same path. The reagent/s-coated coal was contacted with necessary amount of tap water to form the ~65% solid/liquid pulp (*65% stage or homogenization stage*), and diluted to 10 % solid/liquid with tap water (*10% stage*). A final step was the *flotation stage*. During the reagent-coal contact step (adsorption stage), to facilitate good adsorption of the reagents on the coal surface, manual mixing of coal and a reagent in a beaker with a spatula was continued until no aggregates of coal with reagents were noticed. It took usually from 1 to 3 min after each reagent addition.

For a better clarification of the difference between the two versions of direct-contact flotation, a hypothetical test in the presence of 10 g/kg of two reagents (dodecane-$C_{12}E_4$, 5 g/kg each) is considered in Table 14. The reagents are added as anhydrous dodecane, and anhydrous $C_{12}E_4$ for version DCF/A, or 1% (dodecane-$C_{12}E_4$) aqueous solution having the dodecane/$C_{12}E_4$ weight ratio = 1 in version DCF/B.

The reagent/s used in both versions of this procedure together with the investigated parameters are shown in Table 15.

5.4.4. Effect of moisture content on coal flotation

In one series, the direct-contact flotation procedure (DCF) was applied using coal with different moisture contents. The coal moisture content was regulated by a direct exposure of its surface to water-vapor created by the heating of water (Fig. 32).

Table 14. Steps of a hypothetical flotation test carried out applying both versions of direct-contact flotation procedure using 10 g/kg dodecane + $C_{12}E_4$ (5g/kg each). The reagent stocks were either pure chemicals or mixtures of reagents in double distilled water

Direct contact, DCF(A)	**Direct contact, DCF(B)**
1a) coal (100 g dry) is manually mixed with 0.5 g of anhydrous $C_{12}E_4$ (5 g/kg) for 1-3 min until no aggregates are observed Coal (100g) sample + $C_{12}E_4$ (5g/kg)	1) coal (100 g dry) is manually mixed for 1-3 minutes with 100 cm^3 aqueous solution (prepared as 1% by weight (dodecane + $C_{12}E_4$) aqueous stock having dodecane/$C_{12}E_4$ weight ratio of 1, to represent a total dosage of dodecane+$C_{12}E_4$ of 10 g/kg, 5 g/kg each)→ (*contact or adsorption stage*) Coal (100g) + aqueous (dodecane +$C_{12}E_4$) (10g/kg) (*contact or adsorption stage*)
1b) coal from step 1a is manually mixed with 0.5 g of anhydrous dodecane (5 g/kg) for (1-3) min → (*contact or adsorption stage*) coal from step (1a) + dodecane (5g/kg) (*contact or adsorption stage*)	
2) addition of necessary amount of tap water (~150 cm^3) to get a pulp containing ~65% solid/liquid ratio and conditioning for 0.5 min for homogenization → (*65 % or homogenization stage*) Coal from step 1b +water → *"65% stage or homogenization stage"*	2) addition of necessary amount of tap water (~50 cm^3) to get a pulp containing ~65% solid/liquid ratio and conditioning for 0.5 min for homogenization → (*65 % or homogenization stage*) Coal from step 1 + water → *"65% stage or homogenization stage"*
3- addition of necessary dilution tap water (by completing the pulp volume to the cell flotation level) followed by 0.5 min conditioning (*10% stage*)	3- addition of necessary dilution tap water (by completing the pulp volume to the cell flotation level) followed by 0.5 min conditioning (*10% stage*)
4- starting aeration and flotation (*flotation stage*)	4- starting aeration and flotation (*flotation stage*)

Table 15. Summary on reagents and investigated parameters considered during DCF procedure of coal flotation

(DCF/A)

Number of reagents used	Reagent type	Reagent name	Reagent stock	Studied parameter
One reagent	Hydrocarbon	heptane	pure (anhydrous) reagent	dosage of reagent
		dodecane		
	Alcohol	pentanol	pure (anhydrous) reagent	dosage of reagent
		terpineol		
	C_xE_y	$C_{12}E_4$	pure (anhydrous) reagent	dosage of reagent
Two reagents	Hydrocarbon and alcohol	heptane-pentanol	each reagent was separately used as pure (anhydrous)	a) two reagent ratio at 8 g/kg b) two reagent dosage at optimum ratio
		dodecane-pentanol		
	Hydrocarbon and C_xE_y	heptane-$C_{12}E_4$	each reagent was separately used as pure (anhydrous)	a) two reagent ratio at 8 g/kg b) two reagent dosage at optimum ratio
		dodecane-$C_{12}E_4$		
	Alcohol and C_xE_y	$C_{12}E_4$-pentanol	each reagent was separately used as pure (anhydrous)	a) two reagent ratio at 8 g/kg b) two reagent dosage at optimum ratio
Three reagents	Hydrocarbon, C_xE_y and alcohol	dodecane, $C_{12}E_4$ and pentanol	each reagent was separately used as pure (anhydrous)	three reagent ratio at 8 and 16 g/kg

(DCF/B)

Number of reagents used	Reagent type	Reagent name	Reagent stock	Studied parameter
One reagent	Hydrocarbon	dodecane	different wt. % of dodecane in water	dodecane-water forms at a dosage of 10 g/kg
	C_xE_y	$C_{12}E_4$	different wt. % of $C_{12}E_4$ in water	$C_{12}E_4$-water forms at a dosage of 10 g/kg
Two reagents	Hydrocarbon and C_xE_y	dodecane-$C_{12}E_4$	different dodecane-$C_{12}E_4$-water concentrations	two-reagent-water forms at a dosage of 10 g/kg

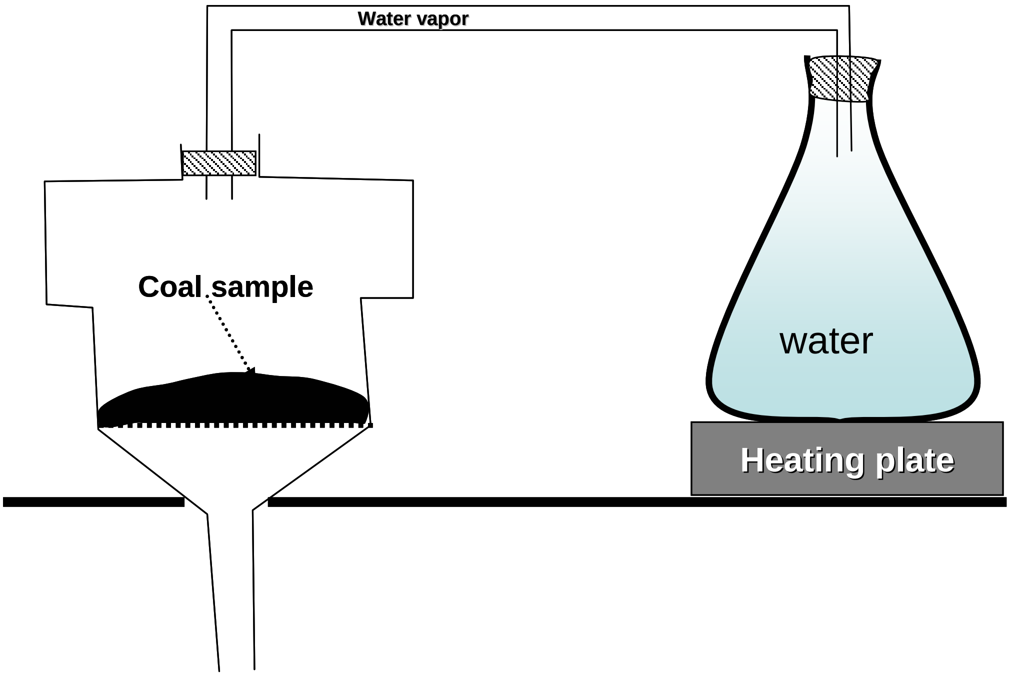


Fig. 32. Moisture regulating system

About 150 g of previously dried flotation feed coal was kept for a certain time in the above system and it was manually homogenized each 5 min. After the intended time, the moisten coal was kept in a closed dessicator, a 5 g of which was taken for the moisture measurement. Based on the sample moisture content, the weight of moist sample containing 100 g of dry coal was calculated and weighted for a given flotation test.

6. Results and discussions

6.1. Phase diagram of hydrocarbon-water-C_xE_y system

In this work, different reagents and their mixtures were used for coal flotation. The reagents and their mixtures are able to form with water different structures (species) which are characterized by phase diagrams. The $C_{12}E_4$-dodecane-water system represents a ternary mixture that is capable to create different structures including microemulsions and is therefore well suited for this study. A diagram for the used-in-this-work $C_{12}E_4$-dodecane-water system at 25 °C is given in Fig. 33(a-b).

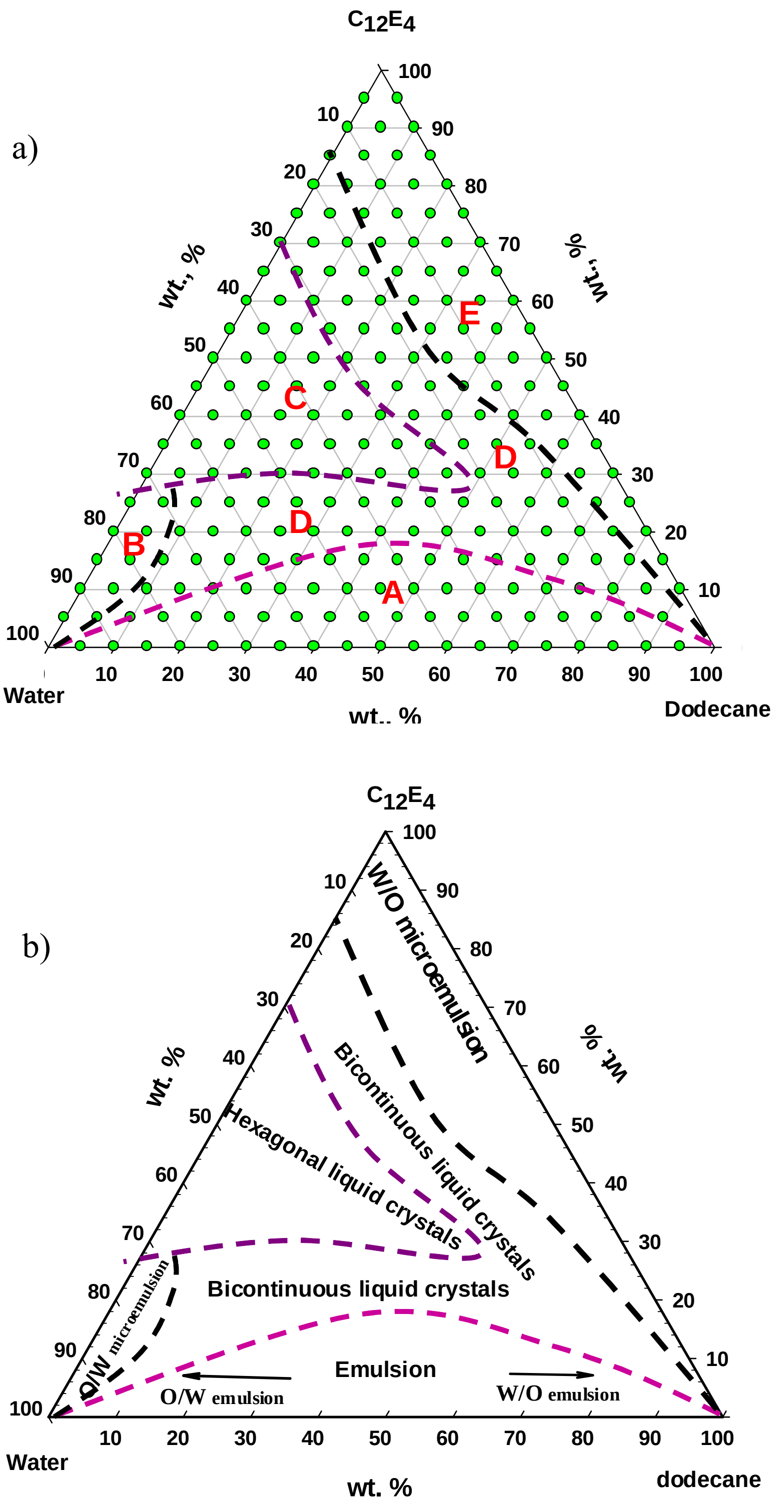


Fig. 33. Ternary phase diagram illustrating different phases formed at different concentrations of water-dodecane-$C_{12}E_4$ system at 25°C (in weight %).

a) circles represent investigated concentrations while dashed lines represent approximate boundaries between different phases. A) different emulsions, B) normal micelles and O/W microemulsions (border between the sub-areas is not shown), C) hexagonal liquid crystals, D) bicontinuous liquid crystals, E) inverted micelles and W/O microemulsions (border between the sub-areas is not shown)

b) names of the phases

The reagent concentrations are given in percent on the weight basis. In Figure 33a, circles represent different studied concentrations of reagents used to construct the phase diagram. Dashed lines represent the approximate borders between different structures. The approximate boundaries were based on visual inspection of the phases created during experiments using UV spectra and literature data. From Figure 33(a-b), one can notice the existence of five different areas containing sub-areas inside each of them. The first major area, A, represents a low level of $C_{12}E_4$ concentration in the system that is from 0.0 to a maximum of ~18% with varying levels of both water and dodecane. This area represents emulsion. It is characterized by a turbid, unstable mixture with an excess amount of dodecane or water near the apexes. The left corner, near the water rich apex of the triangle, represents O/W emulsions where the droplets of dodecane are formed in water as a continuous phase having $C_{12}E_4$ molecules at the oil (dodecane)/water interface. The right corner of this area, dodecane rich area, represents the existence of water droplets found in a continuous dodecane phase or W/O emulsions. Inversion between the two sub-areas takes place gradually by increasing the amount of water or dodecane. The second area, B, represents clear aqueous phase, that is solution. It exists at a high water concentration (> 83%) and low concentrations of dodecane (< 10%) and $C_{12}E_4$ (<20%). The structures formed in that area largely resembles the structures formed on the left-hand side of area A, with the main difference on the formed droplet size. It contains both normal micelles and O/W microemulsion sub-areas. The border between them is not shown. Increasing the $C_{12}E_4$ level results in the formation of a third area, that is area C, which represents liquid crystal structure. In this area an ordered crystal-like structures of reagents, mainly hexagonal, are formed in water. At the same time, area D represents another bi-continuous structure, which is also defined as a special disordered form of the liquid crystals of area C. Finally, area E can be described as swollen reverse micelles or W/O microemulsions. This area also starts with reversed micelles with its border not shown in this plot.

The behavior of this system is similar to other oil-water-nonionic surfactant systems (Kunieda and Shinoda, 1982; Buzier and Ravey, 1983; Fletcher and Morris, 1995; Giasson et al., 1998; Grätz et al., 1998; Forgiarini, 2000). The main features are the same. The system contains all possible species and forms and can be useful for investigating their role in flotation of difficult-to-float oxidized coal.

6.2. Coal flotation applying normal-contact flotation procedure (NCF)

6.2.1. Flotation results using normal-contact flotation procedure (NCF) version A

6.2.1.1. NCF/A of coal in the presence of a single reagent

A series of normal flotation procedure (NCF/A) experiments was run using six different reagents (heptane, dodecane, $C_{12}E_4$, $C_{16}E_{23}$, pentanol, and terpineol) in a single-reagent scheme. The 1 % reagent stock was added to the coal aqueous pulp in different amounts to have different dosages of the reagent. Figure 34 shows clean coal yields and its corresponding ash content at the different studied dosages of each reagent.

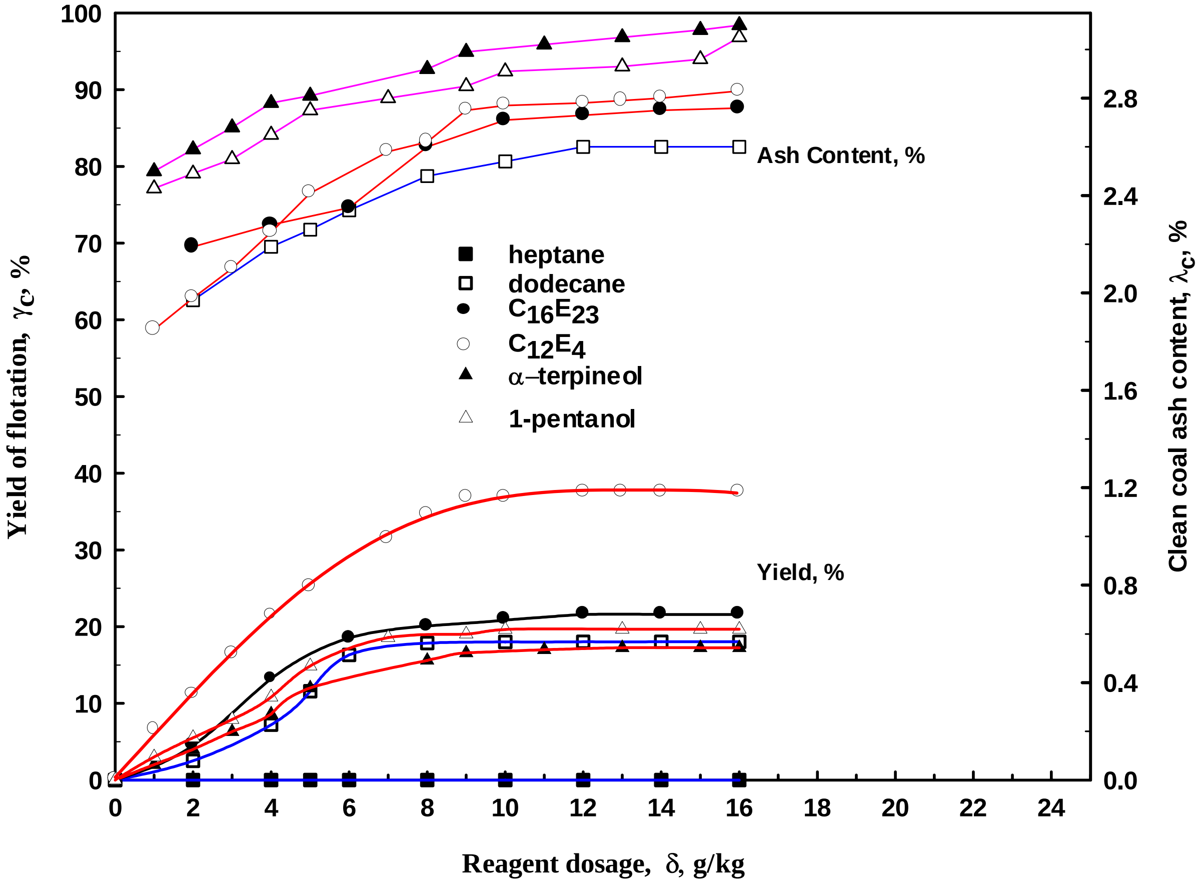


Fig. 34. Effect of reagent type and its dosage on clean coal yield and its ash content applying normal flotation procedure (NCF/A). Each point represents a separate flotation test

It shows, taking into account the reagent dosage of 10 g/kg, that the yield of clean coal was increasing in the following order (yields are given in parentheses in %):

heptane (0)<terpineol (16.6)<dodecane (18)<pentanol (19.5)<$C_{16}E_{23}$ (21)<<$C_{12}E_4$ (37)

(Effect of dosage of one-reagent on clean coal yield at 10 g/kg) (3)

On the other hand, the clean coal ash content at the same dosage (10g/kg) was increasing in a slightly different order that is (clean coal ash contents are given in parentheses in %):

dodecane (2.54)<$C_{16}E_{23}$ (2.71)<$C_{12}E_4$ (2.77)<pentanol (3.0)<terpineol (3.04)

(Effect of dosage of one-reagent on clean coal ash content at 10 g/kg) (4)

The poor flotation response represented by low clean coal yield and high ash content obtained in this series proves that applied coal is a difficult-to-float material. The results also showed that:

- used coal is of low hydrophobicity, and thus frothing action generated by alcohols was not enough to get reasonable yields.
- applied alcohols have low collecting power when used in flotation of used-in-this-study difficult-to-float coal, although previous research revealed their possible adsorption on coal surfaces (Pradip and Fuerstenau, 1982).
- order of reagents regarding obtained clean coal yield did not coincide with the order regarding the clean coal ash contents. The highest clean coal yield in this series was reported using $C_{12}E_4$, and the cleanest coal was obtained using dodecane.

Since the clean coal yield and ash content arrangements of reagents are not the same, there is a need to look for flotation selectivity which would take into account both parameters. It can be accomplished by plotting the Fuerstenau upgrading curve. Table 16 shows a typical (for this work) mass balance (considering dodecane at a dosage range from 2 to 8 g/kg) used to calculate parameters to be plotted as the Fuerstenau curve.

Table 16. Typical, for this work, mass balance of results obtained using different dosages of dodecane (analyses are on moisture free bases)

Dosage g/kg	Product	Yield %	Assay, %		Recovery, %	
			ash	combustible matter	ash	combustible matter
2.0	concentrate	2.50	1.97	98.03	1.30	2.55
	tailing	97.50	3.83	96.17	98.70	97.45
	feed	100.0	3.78	96.22	100.0	100.0
4.0	concentrate	7.20	2.19	97.81	4.14	7.32
	tailing	92.80	3.94	96.06	95.86	92.68
	feed	100.0	3.81	96.19	100.0	100.0
5.0	concentrate	11.60	2.26	97.74	6.89	11.74
	tailing	88.40	3.99	96.01	93.11	88.26
	feed	100.0	3.79	96.21	100.0	100.0
6.0	concentrate	16.30	2.34	97.66	10.04	16.55
	tailing	83.70	4.08	95.92	89.96	83.45
	feed	100.0	3.80	96.20	100.0	100.0
8.0	concentrate	17.85	2.48	97.52	11.62	18.10
	tailing	82.15	4.10	95.90	88.38	81.90
	feed	100.0	3.81	96.19	100.0	100.0

Figure 35 represents Fuerstenau's plot for the one-reagent flotation series. By intuition, one can say that $C_{12}E_4$ provides the highest separation efficiency of the used reagents as for the recovery is concerned. Its yield was the highest while ash content was average. To have a numerical comparison of separation efficiency encountered with each reagent, approximation was run using one-parameter equation (Eq. 2B from Table 8). According to the obtained selectivity indexes, the different reagents can be arranged as follows (number in parenthesis show selectivity index B, able to assume values from 0 to 1):

terpineol (0.053)<pentanol (0.079)<$C_{16}E_{23}$ (0.129)<dodecane (0.139)<$C_{12}E_4$ (0.172)

(Effect of one-reagent dosage on selectivity index B) (5)

The selectivity obtained with $C_{12}E_4$ (B=0.172) agree with conclusions of Jia et al. (2000; 2002) who recommended special reagents (like C_xE_y) for flotation of low rank and oxidized coals. It can be further explained with other literature results (Saleh and Iskra, 1997a) that both hydrophilic and hydrophobic moieties of C_xE_y play role when they are used in flotation. This is why $C_{16}E_{23}$ did not give the same results as $C_{12}E_4$. It should be however stressed that applying $C_{12}E_4$ gives best result in the series but still poor flotation results regarding this coal. Generally, this series showed that the use of a single reagent leads to a limited maximum yield. At the same time, increasing the reagent dosage above 10g/kg level did not provide any significant improvement in neither clean coal yield nor its ash content. This in turn reflects inability to achieve successful results of flotation with oxidized coals using the one-reagent normal flotation approach.

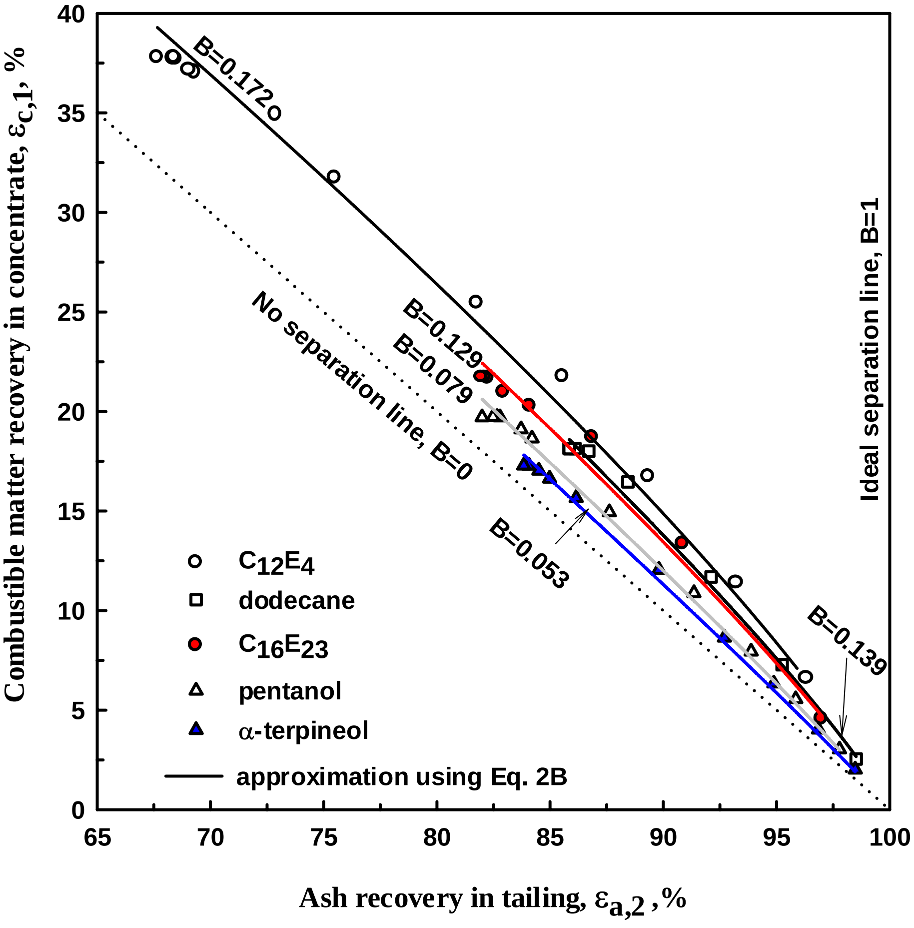


Fig. 35. Fuerstenau's plot showing effect of reagent dosage on the separation of coal applying NCF/A procedure. Each point represents separate test using a certain dosage. The results obtained with each reagent were approximated using Eq. 2B as a series providing single selectivity index B

6.2.1.2. NCF/A of coal in the presence of two reagents

Reagent mixtures usually enhance the performance of coal flotation. In this section, the effectiveness of two-reagent systems in oxidized coal flotation will be discussed. The normal-contact flotation version A (NCF/A), based on one-by-one mode of reagent addition during the adsorption step, will be considered. Each reagent stock was 1% (by wt.) in distilled water.

The two-reagent systems were investigated in three series according to the type of the two reagents used simultaneously. The first series was the hydrocarbon-alcohol systems. The second one investigated the addition of alkyl poly(ethylene glycol) ethers (C_xE_y) and hydrocarbons, while the third series paid attention to the alkyl poly(ethylene glycol) ethers (C_xE_y) and alcohol systems.

The first series involved hydrocarbon and alcohol, forming the following two-reagent systems: heptane–pentanol, dodecane–pentanol, heptane–α-terpineol, and dodecane–α-terpineol. Considering hydrocarbon as collector and alcohol as frother, the NCF/A procedure was conducted in the following sequence: coal → tap water → conditioning → hydrocarbon (collector) → conditioning → alcohol (frother) → conditioning, followed by dilution, aeration and flotation.

To reduce the number of experiments, the dosage of hydrocarbon + alcohol was first constant at 4 g/kg, that is at 40% of the maximum effective dosage in the previously investigated one-reagent systems and the alcohol/hydrocarbon ratio was varied. Figure 36 shows the clean coal yield obtained at the investigated alcohol/hydrocarbon ratios (at 4g/kg). It shows that a maximum clean coal yield was usually reached at the alcohol/hydrocarbon ratio of 1:4 for all of the investigated systems. The clean coal yields (given as numbers in parenthesis expressed in wt. %) obtained at the optimum ratio can be arranged in the following order:

$$\frac{\textbf{heptane+}}{\textbf{+ terpineol}}\textbf{(22.8)} < \frac{\textbf{heptane+}}{\textbf{+ pentanol}}\textbf{(25.1)} < \frac{\textbf{dodecane+}}{\textbf{+ terpineol}}\textbf{(28.9)} < \frac{\textbf{dodecane+}}{\textbf{+ pentanol}}\textbf{(32.1)}$$

$$\text{(Hydrocarbon/alcohol ratio \textasciitilde 4:1 at constant dosage 4g/kg)} \qquad (6)$$

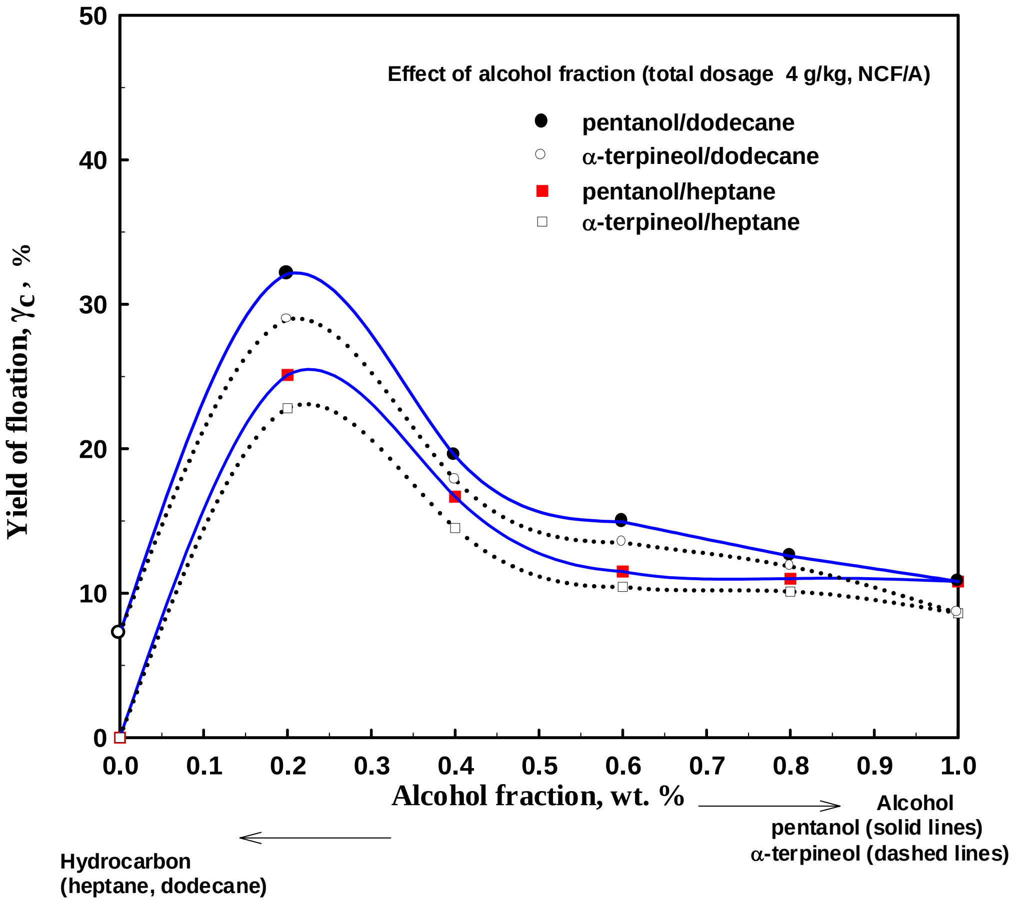


Fig. 36. Effect of alcohol/hydrocarbon ratio on clean coal yield at a total dosage of 4 g/kg of two reagents applying normal-flotation procedure (NCF/A)

The higher clean coal yield obtained when using pentanol with both heptane and dodecane than that obtained using α-terpineol with the same hydrocarbons can be explained by certain collecting power of pentanol alcohol, and its greater foamability (Laskowski, 1998). The order regarding the clean coal ash content (given in parenthesis, %) at the 1:4 ratio for 4g/kg constant dosage was as follows:

$$\frac{\textbf{heptane+}}{\textbf{+pentanol}}\textbf{(2.94)} > \frac{\textbf{heptane+}}{\textbf{+terpineol}}\textbf{(2.75)} > \frac{\textbf{dodecane+}}{\textbf{+terpineol}}\textbf{(2.55)} > \frac{\textbf{dodecane+}}{\textbf{+pentanol}}\textbf{(2.50)}$$

$$\text{(Hydrocarbon/alcohol ratio ~4:1 at constant dosage 4g/kg)} \qquad (7)$$

Separation characteristics for the two-reagent systems included in this series are shown in Fuerstenau's plot (Fig. 37).

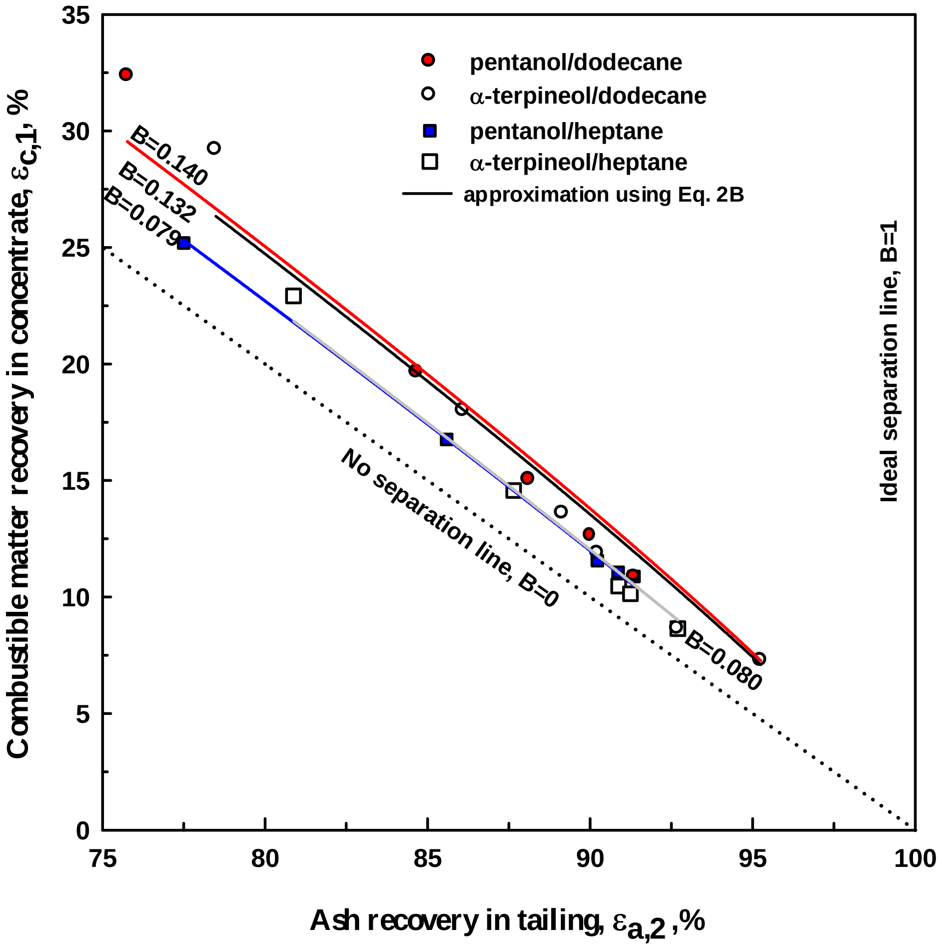


Fig. 37. Fuerstenau's plot showing effect of alcohol/hydrocarbon ratio on separation of coal at total dosage of two reagents of 4g/kg applying NCF/A procedure. Ratios can be read from Fig. 36

Figure 37 shows also that the selectivity order of the two-reagent systems is as follows (values of selectivity index B is given in parenthesis):

$$\frac{\textbf{heptane+}}{\textbf{+ pentanol}}\textbf{(0.079)} \sim = \frac{\textbf{heptane+}}{\textbf{+ terpineol}}\textbf{(0.080)} < \frac{\textbf{dodecane+}}{\textbf{+ terpineol}}\textbf{(0.132)} < \frac{\textbf{dodecane+}}{\textbf{+ pentanol}}\textbf{(0.140)}$$

(Hydrocarbon/alcohol ratio at constant dosage 4g/kg) (8)

The selectivity indices observed in this series were similar to that obtained with individual reagents pointing to a poor flotation separation.

After establishing the optimum alcohol/hydrocarbon ratio, it was worthwhile to investigate the effect of the dosage of the two reagents. Therefore, the total two-reagent dosage was varied, at constant optimum predetermined alcohol/hydrocarbon ratio of 1:4. Figure 38 shows the obtained clean coal yield from this series. The clean coal yields for the two-reagent system series follow the same trend as previously observed with the one-reagent system series. This trend is characterized by an increase in clean coal yield with increasing the total reagent dosage with a plateau after a certain reagent dosage reflecting constant clean coal yield regardless of further increase in the reagent dosage.

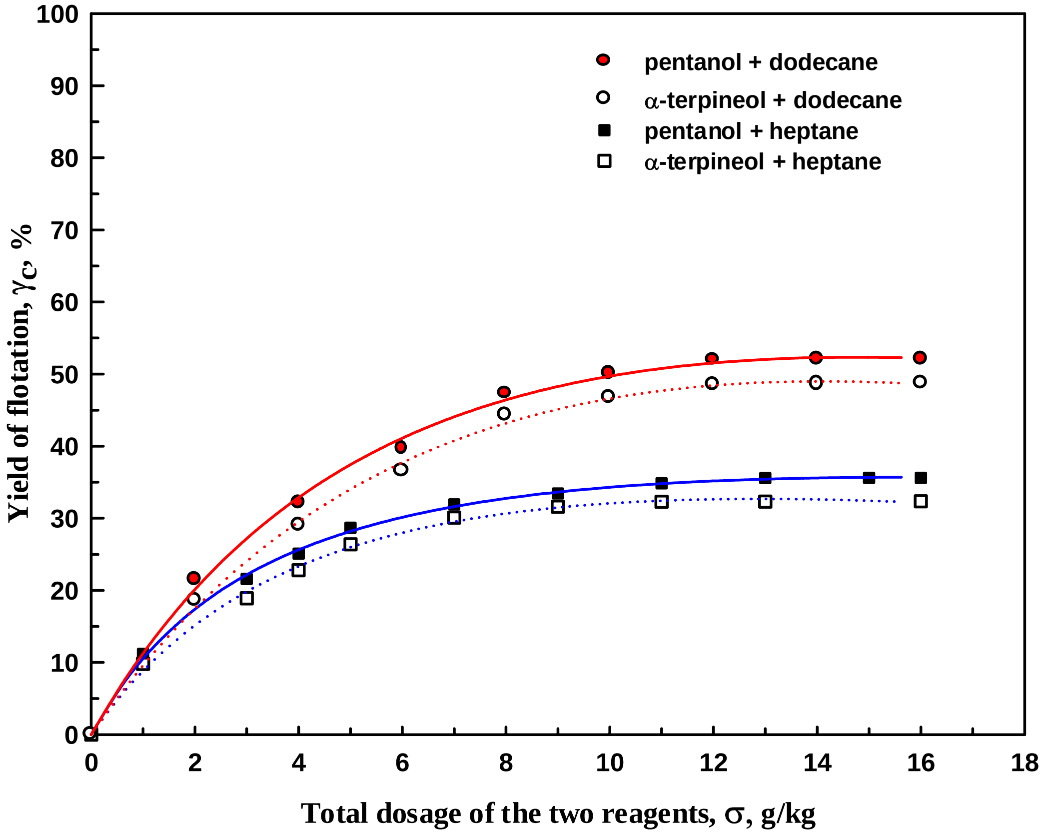


Fig. 38. Effect of hydrocarbon and alcohol system dosage on clean coal yield at optimum alcohol/hydrocarbon ratio (1:4) applying NCF/A procedure

The clean coal yield at the plateau dosage (10 g/kg) (given values in parenthesis in %) can be ordered as follows:

$$\frac{\textbf{heptane+}}{\textbf{+ terpineol}}(\sim 31) < \frac{\textbf{heptane+}}{\textbf{+ pentanol}}(\sim 34) < \frac{\textbf{dodecane+}}{\textbf{+ terpineol}}(46.7) < \frac{\textbf{dodecane+}}{\textbf{+ pentanol}}(50.1)$$

(Hydrocarbon+alcohol at dosage of 10 g/kg at constant ratio ~4:1) (9)

Figure 39 shows a comparison between the different systems regarding their selectivity using the Fuerstenau plot and approximation of the different plotted series using Eq. 2B, from Table 8.

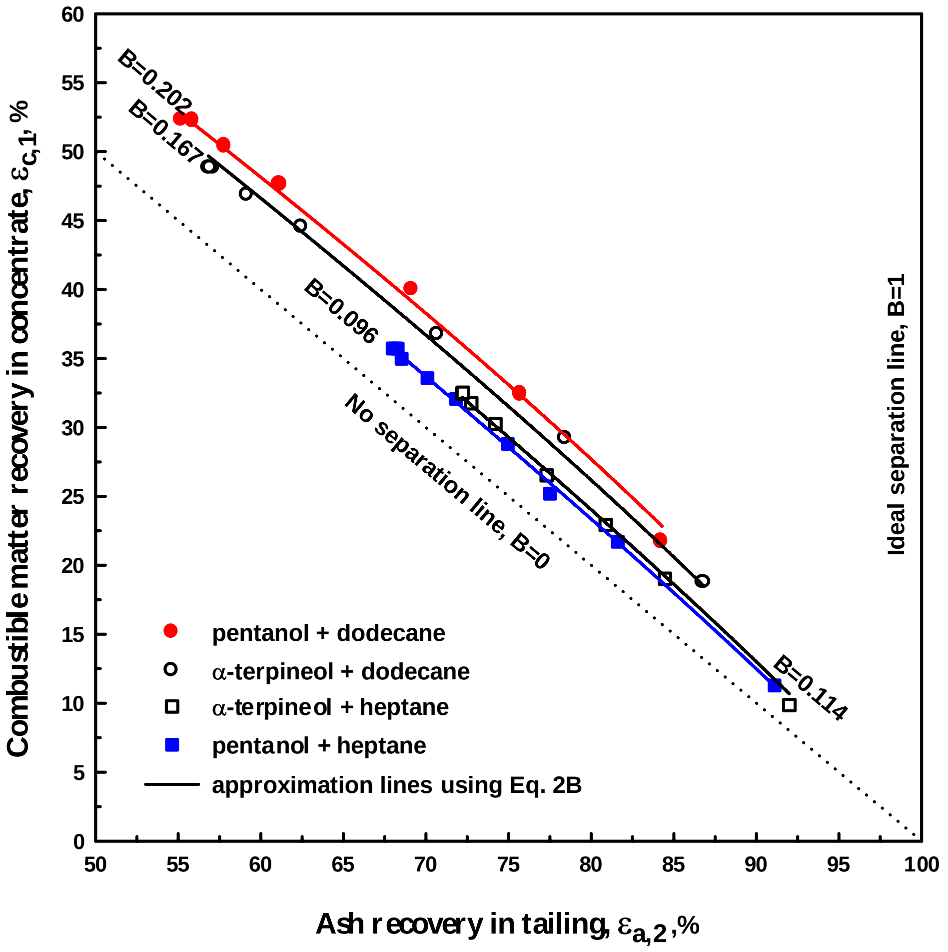


Fig. 39. Fuerstenau's plot showing effect of alcohol + hydrocarbon dosage on the separation of coal at their optimum 1:4 ratio applying NCF/A procedure. Dosages can be read from Fig. 38

Figure 39 and approximation results show that the systems order was as follows (B values in parenthesis):

$$\frac{\text{heptane+}}{\text{+pentanol}}(0.096) < \frac{\text{heptane+}}{\text{+terpineol}}(0.114) < \frac{\text{dodecane+}}{\text{+terpineol}}(0.167) < \frac{\text{dodecane+}}{\text{+pentanol}}(0.202)$$

(Hydrocarbon + alcohol dosage at constant ratio ~4:1) (10)

The series given by Eq. 10 shows the same selectivity trend previously noticed in the case of changing the alcohol/hydrocarbon ratio (series shown by Eq. 8), but the absolute values were higher in the latter case.

The second series of the two-reagent normal-flotation systems involved hydrocarbons with alkyl poly(ethylene glycol) ethers (C_xE_y). It included the following two-reagent systems: heptane–$C_{12}E_4$, dodecane–$C_{12}E_4$, heptane–$C_{16}E_{23}$, and dodecane–$C_{16}E_{23}$. In this series separate reagent stocks were prepared as 1% reagents in double distilled water.

The C_xE_y/hydrocarbon ratio was studied at a total dosage level of 4 g/kg. Figure 40 shows the clean coal yields obtained in this series. It shows also that the optimum C_xE_y/hydrocarbon ratio was 1:4 for all systems. At the optimum C_xE_y/hydrocarbon ratio, the clean coal yield can be ordered as follows (clean coal yields % in parenthesis):

$$\frac{\textbf{heptane} +}{+\,\mathbf{C_{16}E_{23}}}\mathbf{(20.86)} < \frac{\textbf{dodecane} +}{+\,\mathbf{C_{16}E_{23}}}\mathbf{(26.8)} < \frac{\textbf{heptane} +}{+\,\mathbf{C_{12}E_{4}}}\mathbf{(28.3)} < \frac{\textbf{dodecane} +}{+\,\mathbf{C_{12}E_{4}}}\mathbf{(35)}$$

(C_xE_y/hydrocarbon ratio ~1:4 at constant dosage of 4 g/kg) (11)

The maximum clean coal yields obtained in this series are higher than the corresponding maximum clean coal yields obtained in case of hydrocarbon–alcohol systems. This shows the collecting power of the ethoxy compounds in addition to their frothing action.

Figure 41 shows Fuerstenau's plot reflecting separation encountered in this series. The systems preference may be arranged as follows (B values are in parenthesis):

$$\frac{\textbf{heptane} +}{+\,\mathbf{C_{16}E_{23}}}\mathbf{(0.004)} < \frac{\textbf{dodecane} +}{+\,\mathbf{C_{16}E_{23}}}\mathbf{(0.159)} < \frac{\textbf{heptane} +}{+\,\mathbf{C_{12}E_{4}}}\mathbf{(0.215)} < \frac{\textbf{dodecane} +}{+\,\mathbf{C_{12}E_{4}}}\mathbf{(0.253)}$$

(C_xE_y/hydrocarbon ratio at constant dosage of 4 g/kg) (12)

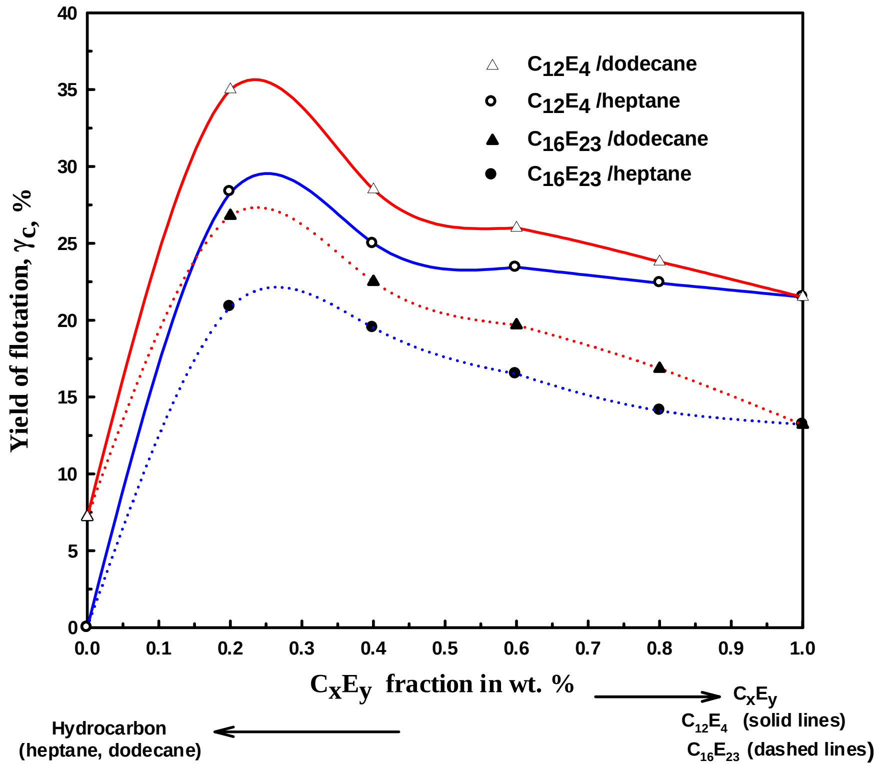


Fig. 40. Effect of C_xE_y fraction in hydrocarbon on flotation of coal at total dosage of 4 g/kg of two reagents using NCF/A procedure

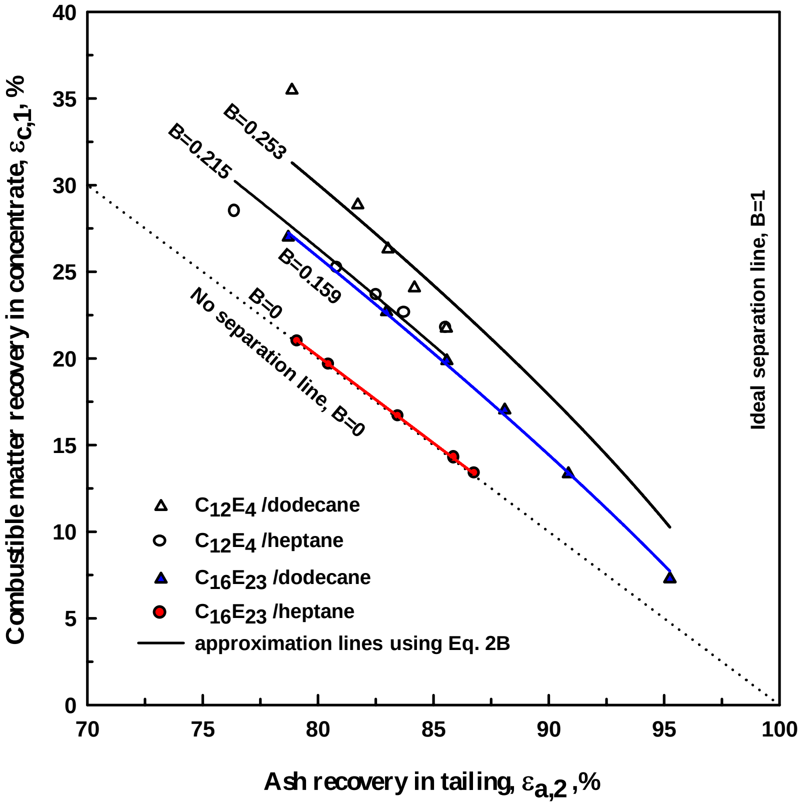


Fig. 41. Fuerstenau's plot showing effect of C_xE_y fraction in hydrocarbon on the separation of coal at total dosage of 4 g/kg using NCF/A procedure. Fractions can be read from Fig. 40

Equation 12 shows that the dodecane–$C_{12}E_4$ system provided the highest separation efficiency in this series. This maybe attributed to the same hydrocarbon chain length present in both of the two reagents (12 carbon atoms each) resulting in a noticeable compatibility between dodecane and $C_{12}E_4$.

Figure 42 illustrates effect of the total dosage of the same two-reagent systems included in the previous series, at the optimum alkyl poly(ethylene glycol) ethers (C_xE_y)/hydrocarbon ratio (1:4) on the obtained clean coal yields. It also reflects the same trend noticed with the hydrocarbon–alcohol systems. The clean coal yields (given in parenthesis in %) obtained in this series (at a total dosage of 10 g/kg) were:

$$\frac{\textbf{heptane +}}{\textbf{+ C}_{16}\textbf{E}_{23}}\,\textbf{(31.3)} < \frac{\textbf{dodecane +}}{\textbf{+ C}_{16}\textbf{E}_{23}}\,\textbf{(34.8)} < \frac{\textbf{heptane +}}{\textbf{+ C}_{12}\textbf{E}_{4}}\,\textbf{(41.25)} < \frac{\textbf{dodecane +}}{\textbf{+ C}_{12}\textbf{E}_{4}}\,\textbf{(45.21)}$$

$$(C_xE_y/\text{hydrocarbon dosage 10 g/kg at constant ratio} \sim 1{:}4) \tag{13}$$

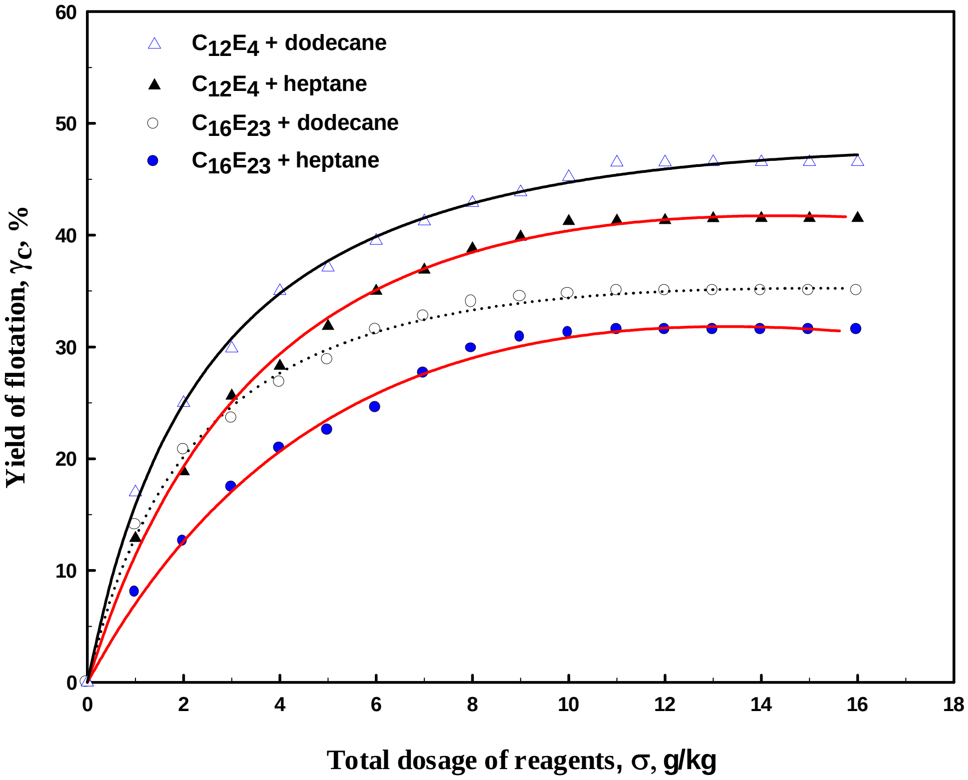


Fig. 42. Effect of hydrocarbon and C_xE_y dosage on clean coal yield at optimum C_xE_y/hydrocarbon ratio (1:4) using NCF/A procedure

Figure 43 shows Fuerstenau's plot reflecting separation phenomena corresponding to the different two-reagent systems involved in this series. Systems selectivity index B (given in parenthesis) was as follows:

$$\frac{\textbf{heptane +}}{\textbf{+ } \mathbf{C_{16}E_{23}}}\textbf{(0.096)} < \frac{\textbf{heptane +}}{\textbf{+ } \mathbf{C_{12}E_{4}}}\textbf{(0.123)} < \frac{\textbf{dodecane +}}{\textbf{+ } \mathbf{C_{16}E_{23}}}\textbf{(0.129)} < \frac{\textbf{dodecane +}}{\textbf{+ } \mathbf{C_{12}E_{4}}}\textbf{(0.256)}$$

(C_xE_y/hydrocarbon dosage at constant ratio ~1:4) (14)

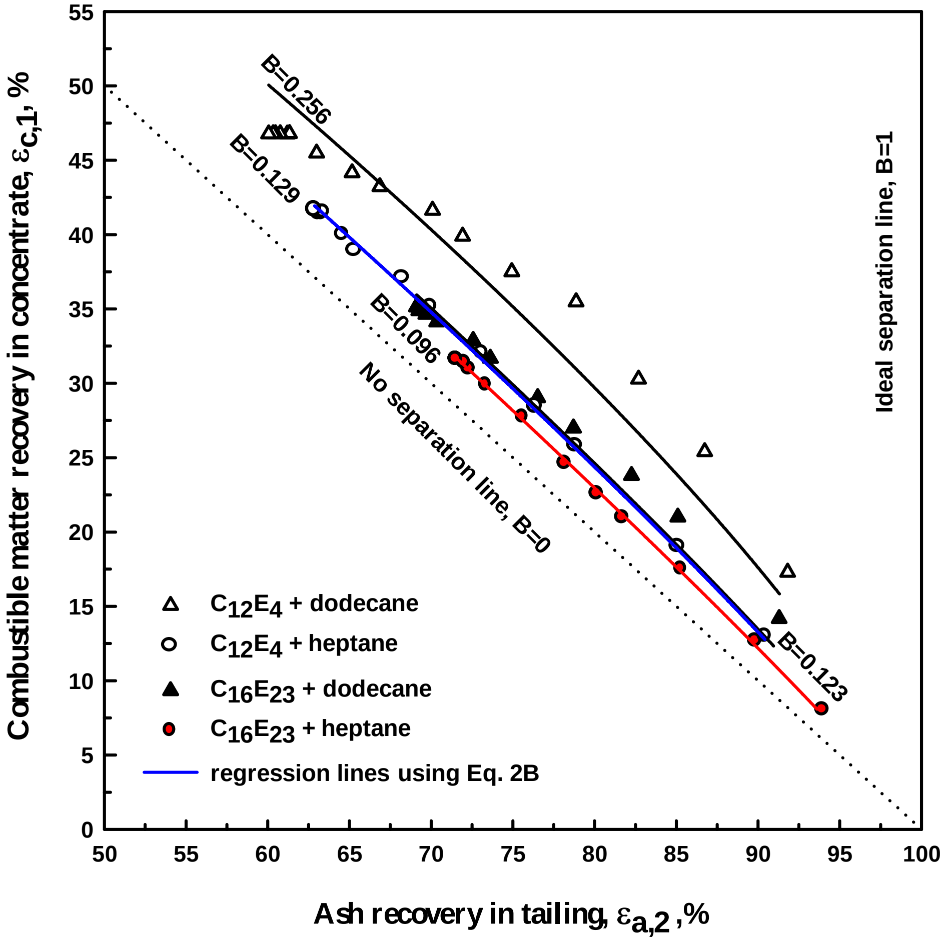


Fig. 43. Fuerstenau's plot showing effect of C_xE_y + hydrocarbon dosage on separation of coal at optimum C_xE_y/hydrocarbon ratio (1:4) applying NCF/A procedure. Dosages can be read from Fig. 42

The last two-reagent normal-flotation series involved the alkyl poly(ethylene glycol) ether (C_xE_y)–alcohol systems. It contained the following systems: $C_{12}E_4$–pentanol, $C_{12}E_4$–α-terpineol, $C_{16}E_{23}$–pentanol, and $C_{16}E_{23}$–α-terpineol. The reagent feed stocks were prepared separately as 1% by wt. in double distilled water. The required dosage of the ethoxy compound was added first followed by the required dosage of alcohol.

Figure 44 shows the effect of the alcohol/C_xE_y ratio at a total dosage of 4g/kg on the obtained clean coal yields. The optimum alcohol/C_xE_y ratio was 2:3. The optimum ratio in this series is different from that obtained in the two previously studied series (hydrocarbon–alcohol and hydrocarbon–C_xE_y). This maybe attributed to the different nature of interactions between the two-reagents in the system. At the optimum ratio, the clean coal yield (given in parenthesis in %) was as follows:

$$\frac{C_{16}E_{23}+}{+\text{terpineol}}(30.0) < \frac{C_{16}E_{23}+}{+\text{pentanol}}(32.0) < \frac{C_{12}E_{4}+}{+\text{terpineol}}(45.60) < \frac{C_{12}E_{4}+}{+\text{pentanol}}(50.10)$$

(Alcohol/C_xE_y ratio 2:3 at constant dosage of 4g/kg) (15)

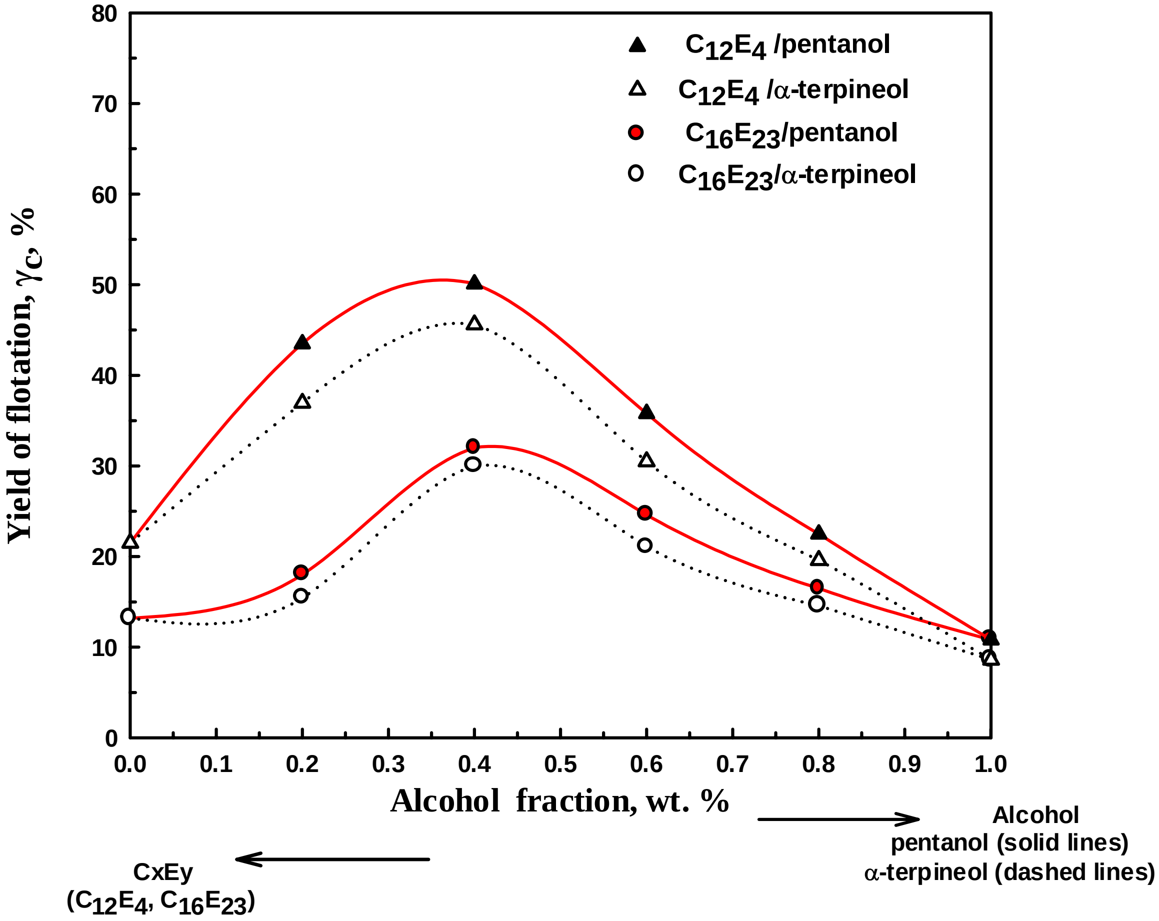


Fig. 44. Effect of alcohol/C_xE_y ratio on clean coal yield at a total dosage of the two reagents of 4 g/kg using NCF/A procedure

It is clear that any $C_{12}E_4$–alcohol system results in higher clean coal yields than the corresponding $C_{16}E_{23}$–alcohol system with the preferential of pentanol alcohol usage over α-terpineol in both cases.

Figure 45 shows Fuerstenau's plot illustrating separation resulting from the different two-reagent systems investigated in this series. Based on the selectivity, the systems have the following arrangement (with selectivity index B value in parenthesis):

$$\frac{\mathbf{C_{16}E_{23}+}}{\mathbf{+terpineol}}\mathbf{(0.141)} \sim= \frac{\mathbf{C_{16}E_{23}+}}{\mathbf{+pentanol}}\mathbf{(0.139)} < \frac{\mathbf{C_{12}E_{4}+}}{\mathbf{+pentanol}}\mathbf{(0.233)} \sim= \frac{\mathbf{C_{12}E_{4}+}}{\mathbf{+terpineol}}\mathbf{(0.237)}$$

(Alcohol/C_xE_y ratio at constant dosage of 4g/kg) (16)

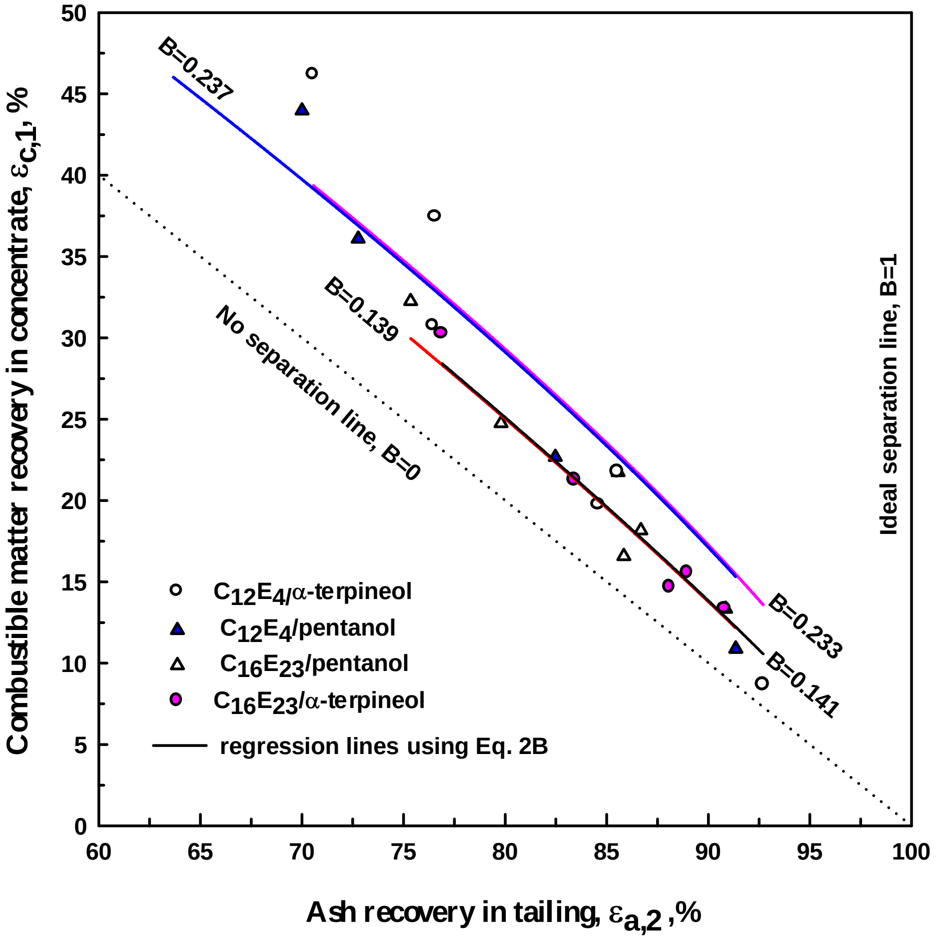


Fig. 45. Fuerstenau's plot showing effect of alcohol/C_xE_y ratio on separation of coal at total dosage of two reagents of 4 g/kg applying NCF/A procedure. Ratios can be read from Fig. 44

Figure 46 illustrates the effect of the total dosage of the two reagents on the clean coal yield obtained using different alkyl poly(ethylene glycol) ether (C_xE_y) and alcohol systems at the optimum predetermined ratio of 2:3. It shows that there exists some improvements in the yield of flotation. The clean coal yields, given in parenthesis in % at a total reagents dosage of 10 g/kg, were as follows:

$$\frac{\mathbf{C_{16}E_{23}+}}{\mathbf{+terpineol}}(\sim 41) < \frac{\mathbf{C_{16}E_{23}+}}{\mathbf{+pentanol}}(42.7) < \frac{\mathbf{C_{12}E_{4}+}}{\mathbf{+terpineol}}(54.6) < \frac{\mathbf{C_{12}E_{4}+}}{\mathbf{+pentanol}}(60.9)$$

(Alcohol+C_xE_y dosage of 10g/kg at constant ratio 2:3) (17)

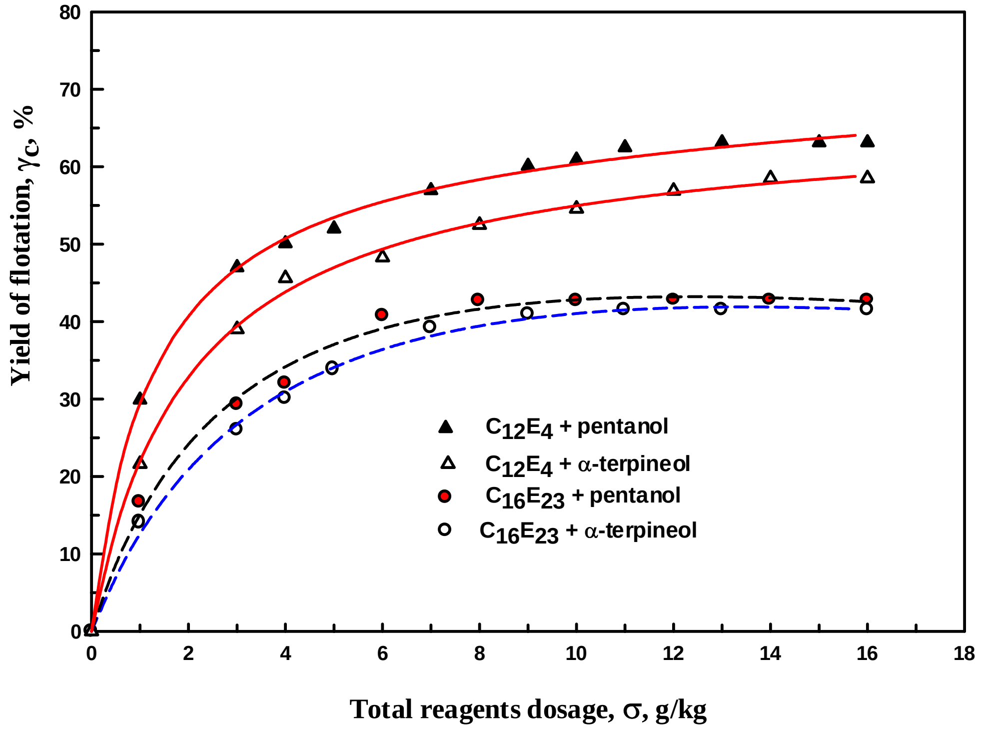


Fig. 46. Effect of C_xE_y and alcohol dosage on flotation yield of clean coal at their optimum ratio (3:2) using normal-flotation procedure (NCF/A)

The arrangement according to selectivity index B (given in parenthesis) was different (Fig. 47) and was as follows:

$$\frac{\mathbf{C_{16}E_{23}+}}{\mathbf{+terpineol}}(0.175) < \frac{\mathbf{C_{16}E_{23}+}}{\mathbf{+pentanol}}(0.184) < \frac{\mathbf{C_{12}E_{4}+}}{\mathbf{+pentanol}}(0.299) \sim= \frac{\mathbf{C_{12}E_{4}+}}{\mathbf{+terpineol}}(0.310)$$

(Alcohol+C_xE_y dosage at constant ratio 2:3) (18)

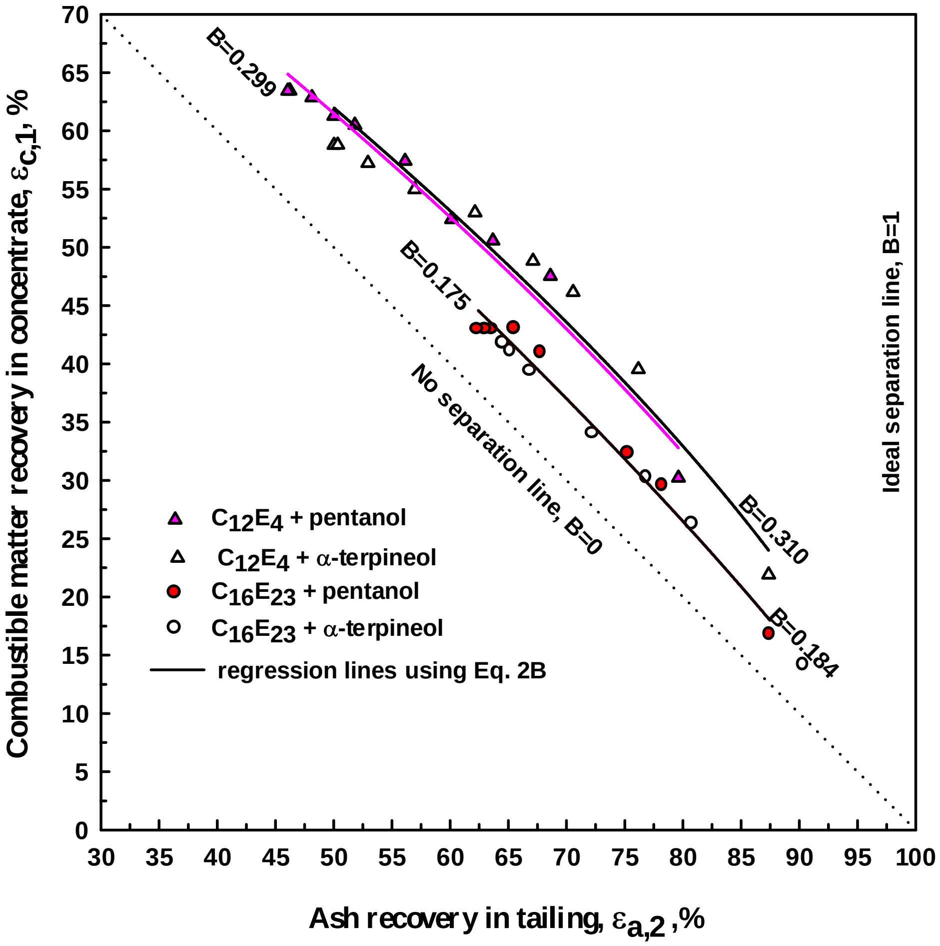


Fig. 47. Fuerstenau's plot showing effect of type and dosage of CxEy and alcohol system, at an optimum C_xE_y/alcohol ratio (3:2) on separation of coal applying normal-contact flotation procedure (NCF/A). The dosage can be read from Fig. 46

For comparing all of the studied systems, Table 17 shows selectivity indices (B) encountered when changing the ratio for all studied two-reagent systems. Basing on this Table, one can say that at 4 g/kg:

- maximum separation was achieved when changing the C_xE_y/hydrocarbon ratio, (dodecane–$C_{12}E_4$ and heptane–$C_{12}E_4$ having selectivity index B of 0.253 and 0.215 respectively). It was followed by changing C_xE_y/alcohol ratio, where the $C_{12}E_4$-pentanol system has a selectivity index B of 0.237 and $C_{12}E_4$-α-terpineol system has a selectivity index B of 0.233.
- all of the other investigated systems provided lower separation having selectivity index B less than 0.16. However, in all cases a substitution of dodecane with any

other reagent (alcohol or C_xE_y) gave better separation than modifying heptane with the same alcohol or C_xE_y reagent.

Table 17. Separation efficiency indices B resulting from varying two-reagent ratio at total dosage of 4 g/kg using normal-contact flotation procedure (NCF/A)

Reagent	heptane	dodecane	$C_{12}E_4$	$C_{16}E_{23}$	pentanol	α-terpineol
heptane	-	-	0.215	0.004	0.079	0.080
dodecane	-	-	0.253	0.159	0.140	0.132
$C_{12}E_4$	0.215	0.253	-	-	0.237	0.233
$C_{16}E_{23}$	0.004	0.159	-	-	0.139	0.141
pentanol	0.079	0.140	0.237	0.139	-	-
α-terpineol	0.080	0.132	0.233	0.141	-	-

Table 18 shows selectivity indices (B) when changing the total dosage of the considered reagent/s. Basing on this Table, one can draw the following conclusions:

- maximum separation was achieved by varying the total dosage of C_xE_y–alcohol systems at their optimum ratio. The $C_{12}E_4$-α-terpineol and $C_{12}E_4$-pentanol systems have the maximum efficiency indices B of this series (0.310 and 0.299, respectively). It is a different system from that resulted in a maximum separation in the case of studying the two reagents ratio (Table 17). This illustrates the fact that not only the ratio between the two reagents is important in determining the separation efficiency but also the total dosage as well
- the hydrocarbon-C_xE_y system followed the above systems regarding separation efficiency. The dodecane-$C_{12}E_4$ two-reagent system resulted in a separation efficiency index B of 0.256
- all other investigated systems resulted in much lower selectivity index B.

Table 18. Effect of one- and two-reagent dosage on separation efficiency indices (B) of coal using normal-contact flotation procedure (NCF/A)

Reagent	heptane	dodecane	$C_{12}E_4$	$C_{16}E_{23}$	pentanol	α-terpineol
heptane	-	-	0.123	0.096	0.096	0.114
dodecane	-	**0.139***	0.256	0.129	0.202	0.167
$C_{12}E_4$	0.123	0.256	**0.172**	-	0.299	0.310
$C_{16}E_{23}$	0.096	0.129	-	**0.129**	0.184	0.175
pentanol	0.096	0.202	0.299	0.184	**0.079**	-
α-terpineol	0.114	0.167	0.310	0.175	-	**0.053**

*Bold numbers represent separation efficiency indices obtained in one-reagent systems

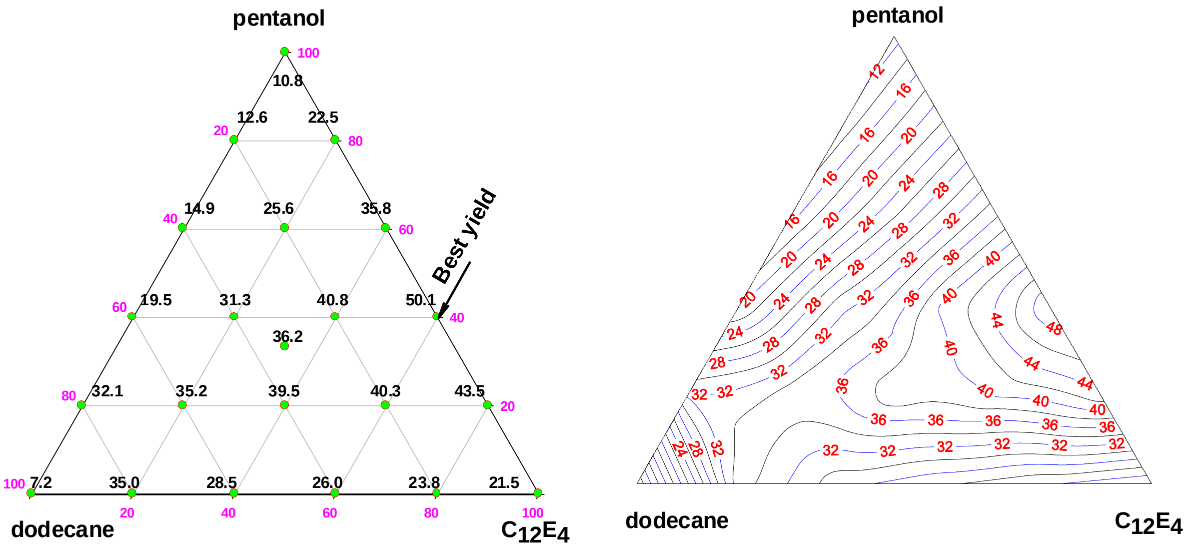
6.2.1.3. NCF/A of coal in the presence of three reagents

The investigated two-reagent coal flotation systems revealed an improvement in clean coal yield and separation over the one-reagent systems. Therefore, a three-reagent system (dodecane-$C_{12}E_4$-pentanol) was investigated applying the normal-contact flotation procedure (version A). The selection of reagents was based on the best separation indices given in Eqs. 3-18. The stocks of used reagents were 1% by weight in distilled water. In a one-by-one mode of addition of reagents, dodecane served as a collector, and thus, it was added first, followed by the needed dosage of $C_{12}E_4$, which served as a promoter, and finally, the necessary pentanol dosage was added keeping in mind that alcohol acts as a frother in this system. The different studied three-reagent combinations are shown in Table 19.

Table 19. Different dodecane-$C_{12}E_4$-pentanol combinations selected for coal flotation applying normal-contact flotation procedure (NCF/A)

Reagent↓ / Exp. #→	Wt. % in the considered combination each of them taken from its prepared stock (1% by weight in double distilled water)						
	1	2	3	4	5	6	7
dodecane	60	40	20	33	40	20	20
$C_{12}E_4$	20	40	60	33	20	40	20
pentanol	20	20	20	34	40	40	60

The three-reagent combinations were investigated at two total dosage levels, that is at 4 and 10 g/kg. Figure 48a illustrates clean coal yields obtained at 4g/kg, together with the suitable results for one and two-reagent systems. One can see in this plot that the clean coal yields obtained from the different studied three-reagent combinations were in the range of ~26 to ~41%. The minimum clean coal yield (25.6% or ~26) was achieved at the dodecane:$C_{12}E_4$:pentanol weight ratio of 1:1:3, while the maximum clean coal yield (~41%) was achieved at two combinations of the three reagents, namely at the dodecane:$C_{12}E_4$:pentanol weight ratios of 1:2:2 and 1:3:1. The ratios indicate a negative effect of pentanol. However, a clean coal yield of 50.1% was achieved using the pentanol-$C_{12}E_4$ two-reagent system at the $C_{12}E_4$:pentanol weight ratio of 3:2. Therefore, it can be said that simultaneous application of 4g/kg of the three reagents, in general, did not show any noticeable improvement regarding clean coal yields. To have a complete view for the three-reagent combinations, a yield contour map was drawn based on data of Fig. 48a using the Surfer V.7 software.



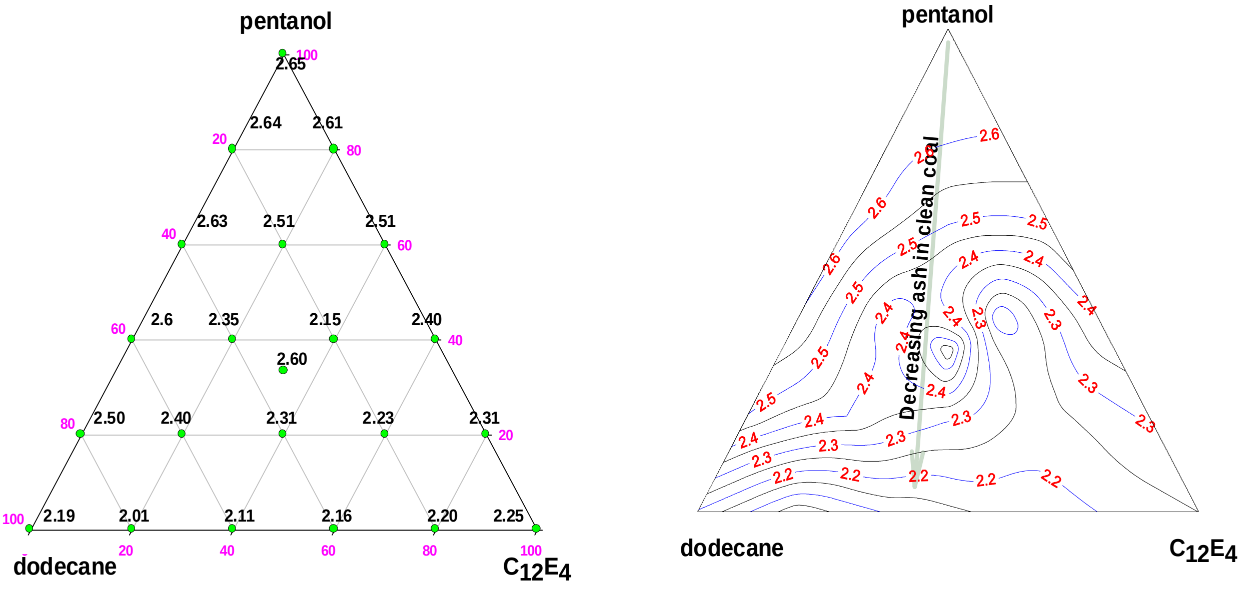
a) clean coal yield response map

b) clean coal yield contour map

Fig. 48. Effect of different combinations of dodecane-$C_{12}E_4$-pentanol three-reagent system on clean coal yield at total dosage of 4 g/kg applying NCF/A procedure. a) response map. Circles indicate studied combinations and values represent clean coal yield, b) contour map of clean coal yield drawn using Surfer V. 7 software based on data from Fig. 48a

Figure 48b shows contours connecting different combinations of the three reagents that provide the same quantity of concentrate regardless of its quality. The contours illustrate that clean coal yields are of low values starting from the plot apexes (one-reagent systems) increasing in the direction of two and three-reagent combinations. The contours are crowded near the apexes that reflect the sensitivity of yield to reagent modification, while the wide gaps among contour lines in the plot center points to an insignificant influence of the three-reagent combinations. This can be attributed to complex interactions occurring among the three reagents in water.

Figure 49a presents the clean coal ash content corresponding to the clean coal yields shown in Fig. 48a at the same dosage level (4g/kg). It shows that the cleanest coal that can be obtained using three-reagent combinations and it has the ash content of 2.15% at the dodecane:$C_{12}E_4$:pentanol ratio of 2:1:2. This is not the same as combinations resulting in the highest clean coal yield. At the same time, equal ratios of the three reagents (1:1:1) lead to the worst clean coal among the studied three-reagent combinations having the ash content of 2.6%. It can be seen from Fig. 49a that the dodecane-$C_{12}E_4$ two-reagent system, when compared to the three reagent combinations, provided a cleaner or the same quality clean coal product having ash content of 2.01, 2.11, and 2.16 %, at the $C_{12}E_4$:dodecane ratios of 1: 4, 2:3 and 3:2, respectively. The highest yield was obtained using the $C_{12}E_4$-pentanol two-reagent system (Fig. 48a), while the cleanest product with lowest ash content was obtained for another two-reagent system (dodecane-$C_{12}E_4$) (Fig. 49a). Using the three-reagent system partially solved this conflict, as there are certain combinations of the three-reagents that may produce clean coal of moderate quality and quantity. The obtained clean coal products have yields slightly lower than the maximum clean coal yield and ash contents somehow higher than the cleanest product ash content.



a) clean coal ash content response map

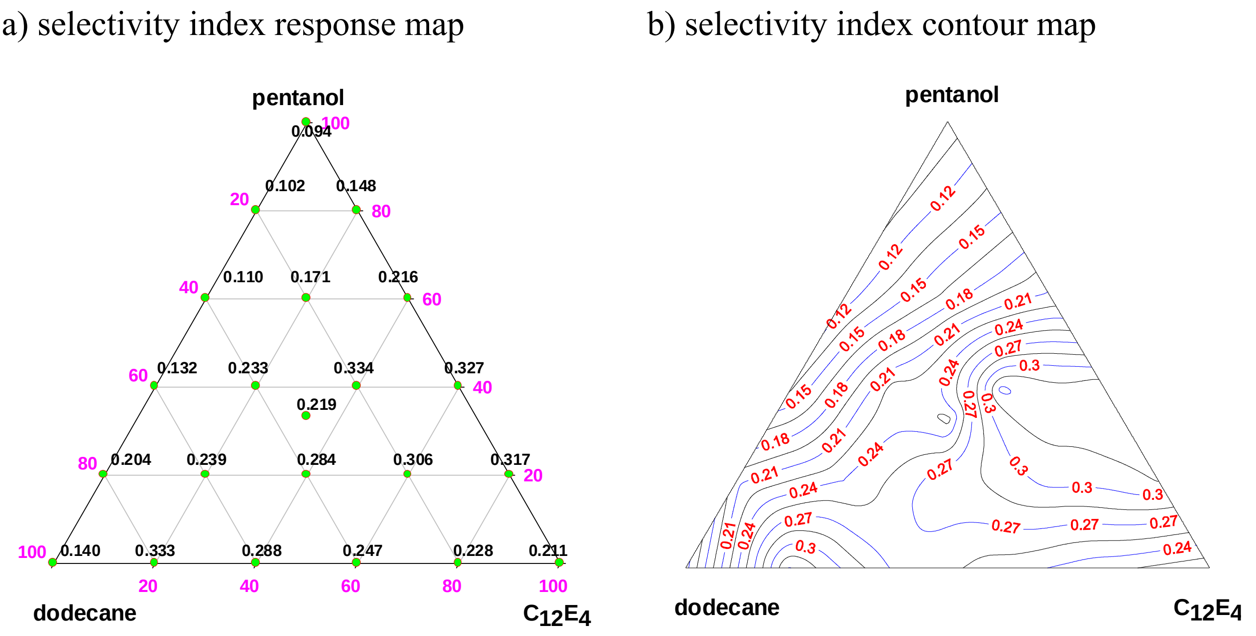
b) clean coal ash content contour map

Fig. 49. Effect of different combinations of reagents (dodecane-$C_{12}E_4$-1-pentanol) on clean coal ash at total dosage of 4 g/kg applying NCF/A procedure. a) response map. Circles indicate studied points and values represent clean coal ash content, b) contour map of clean coal ash drawn from data of Fig. 49a

Figure 49b illustrates clean coal ash contents contour map drawn using data of Figure 49a. The contours in this plot represent reagents combinations that lead to the constant quality of clean coals regardless of their quantity. They show that the high ash content observed with the one-reagent system (pentanol) was decreasing continuously when adding dodecane and/or $C_{12}E_4$. The decreasing trend of clean coal ash contour shows that high proportions of pentanol are harmful to product quality. The gaps between contours indicate sensitivity to reagent combination changes.

In order to evaluate the selectivity of separation in the dodecane-$C_{12}E_4$-pentanol system at the 4g/kg dosage, the results from Figs 48a and 49a were combined to calculate the combustible matter recovery in concentrate and its corresponding ash reject in tailing. The two separation parameters were treated, using the Feurestnau plot and Eq. 2B from Table 8, to determine selectivity index B (Fig. 50). Figure 50a shows that at 4g/kg the different dodecane-$C_{12}E_4$-pentanol three-reagent combinations provided separation efficiency indices ranging from 0.171 (at dodecane:$C_{12}E_4$:pentanol ratio of 1:1:3) to 0.334 (at dodecane:$C_{12}E_4$:pentanol ratio of 1:2:2). At the same time, one-reagent systems (apexes of the plot) resulted in a minimum value of selectivity index B of 0.094 when using 4 g/kg of pentanol alone, while the maximum value of selectivity indices B for the two-reagent systems (outside borders of the plot) were the same as those of three-reagent combinations. The $C_{12}E_4$-dodecane two-reagent system resulted in selectivity index B of 0.333 at the $C_{12}E_4$:dodecane ratio of 1:4 and the two-reagent $C_{12}E_4$-pentanol system provided selectivity index B of 0.327 at the $C_{12}E_4$:pentanol ratio of 3:2.

Figure 50b shows the general trend of the selectivity change with varying the reagents combinations by drawing the iso-selectivity contour lines based on the data from Fig. 50a. It is clear that the poor selectivity encountered when using pentanol alone is being improved when it was substituted by either dodecane or $C_{12}E_4$. The contour lines seem to be parallel and inclined. Their inclination is usually towards the higher dodecane dosage compared to that of $C_{12}E_4$ at comparable selectivity. This in turn reflects the fact that $C_{12}E_4$ is more effective for coal separation than dodecane.



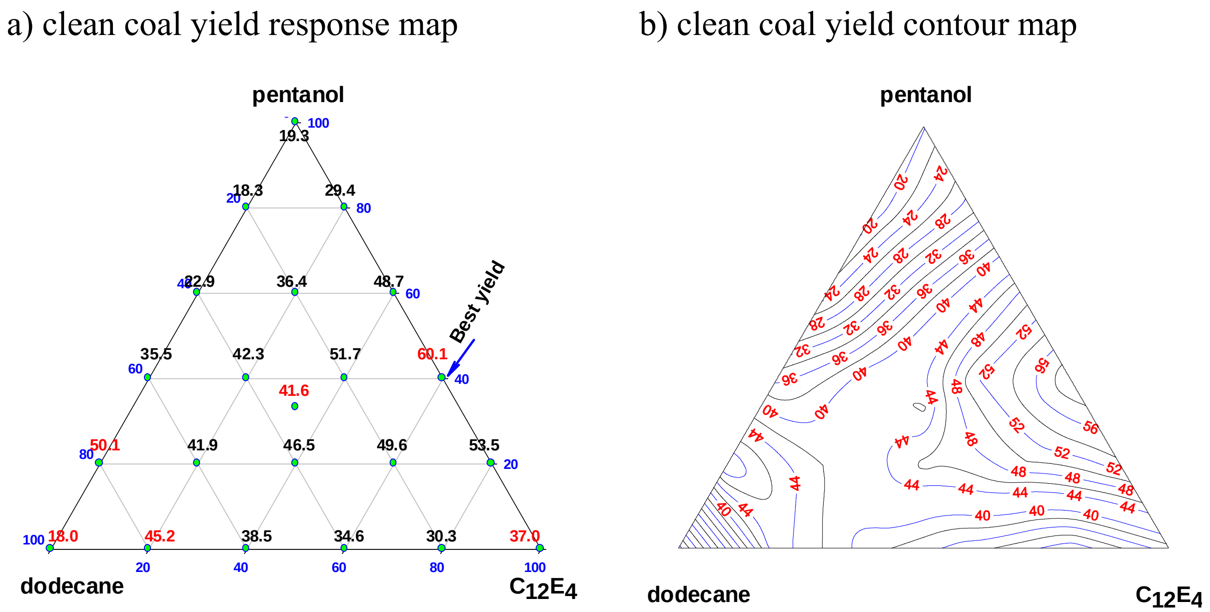
a) selectivity index response map

b) selectivity index contour map

Fig. 50. Effect of dodecane-$C_{12}E_4$-pentanol combinations on clean coal selectivity at total dosage of 4 g/kg applying NCF/A procedure. a) response map. Circles indicate studied combinations and values represent selectivity index B, b) contour map of selectivity index B based on data from Fig. 50a

Figure 51a shows the obtained clean coal yields together with suitable results from one- and two-reagent systems at the 10 g/kg level. It shows that the clean coal yield resulted from the different three-reagent combinations ranges from 36.4%, at the dodecane:$C_{12}E_4$:pentanol ratio of 1:1:3, to 51.7% at the dodecane:$C_{12}E_4$:pentanol ratio of 1:2:2. At this high dosage level, the maximum clean coal yield is equal to 60.1% and was obtained for the $C_{12}E_4$-pentanol two-reagent system at the $C_{12}E_4$:pentanol ratio of 3:2. The three-reagent combinations did not reflect any improvement over that obtained with the two-reagent systems at both considered levels of 4 and 10 g/kg.

Figure 51b shows a yield contour map based on the data from Fig. 51a. In this case, the contours have the same trend as for the 4g/kg level of chemicals. The yield improvement also starts from one reagent (top of the triangle) going towards two- or three-reagent modifications but with some differences regarding the density of contour lines and their values.

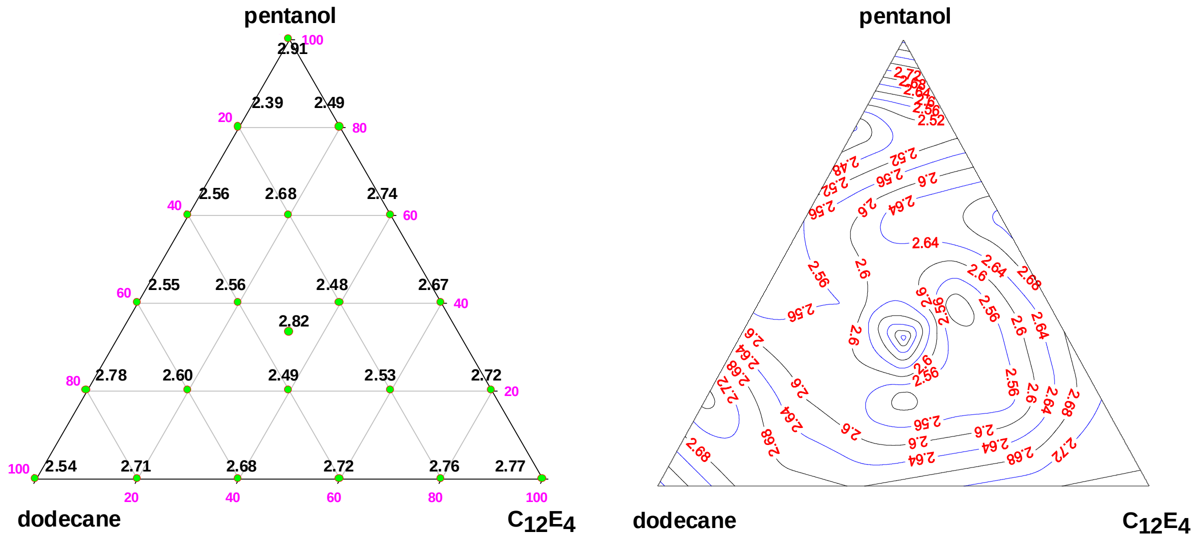

a) clean coal yield response map

b) clean coal yield contour map

Fig. 51. Effect of dodecane-$C_{12}E_4$-pentanol combinations on clean coal yield at total dosage of 10 g/kg applying NCF/A procedure. a) response map. Studied combinations and obtained results, circles indicate studied points and values represent clean coal yield, b) contour map of clean coal yield drawn from data in Fig. 51a

Figure 52a illustrates clean coal ash content obtained from different dodecane-$C_{12}E_4$-pentanol combinations at 10g/kg of reagents together with suitable results of one- and two-reagent systems. The cleanest product resulted from the three-reagent combinations contained 2.48% ash, and was achieved at the dodecane:$C_{12}E_4$:pentanol ratio of 1:2:2. The worst product was again achieved at equal proportions of the three reagents and contained 2.82% ash. Using 10 g/kg of pentanol alone resulted in a product having higher ash content (2.92%). The ash content was decreased when mixing pentanol with either dodecane or $C_{12}E_4$ to form two-reagent systems. Only at the dodecane:pentanol ratio of 1:4 a product of a better quality compared to the three-reagent products was obtained because it contained 2.39% of ash. This in turn confirms that the dodecane-pentanol two-reagent system is better than any dodecane-$C_{12}E_4$-pentanol combination regarding the product ash content.

Figure 52b shows clean coal ash contour map based on the data of Fig. 52a. The contours trend is completely different from that noticed at the lower (4 g/kg) level of chemicals (Fig. 49b). In this case, the contours are of higher values which show that at the higher level of reagents the products are of lesser quality. The contour lines are crowded at the one-reagent apexes (pentanol and dodecane) and form wide gaps at the $C_{12}E_4$ apex. The contours at the center show different trends from completely crowded to completely spread pointing to complex interactions among the three reagents.

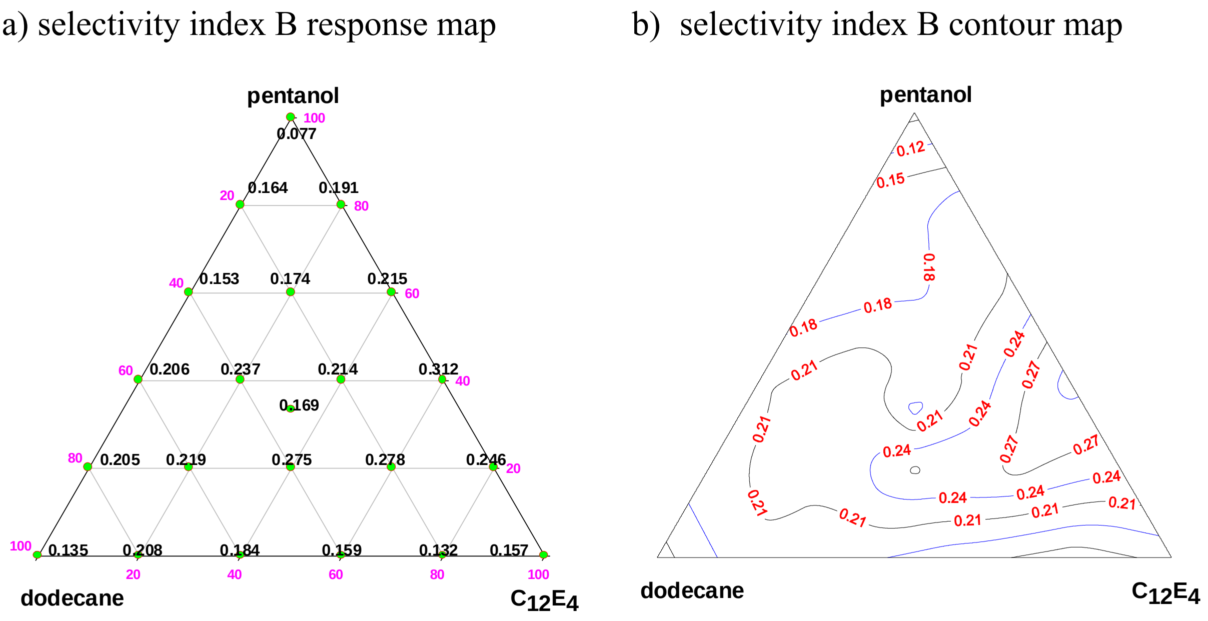


a) clean coal ash content response map

b) clean coal ash contour map

Fig. 52. Effect of dodecane-$C_{12}E_4$-pentanol combinations on clean coal ash content at total dosage of 10 g/kg applying NCF/A procedure. a) response map showing studied combinations and obtained results. Circles indicate studied points and values represent clean coal ash content, b) contour map of clean coal ash drawn from data in Fig. 52a

Figure 53a shows separation related with this three-reagent system at the studied level of 10 g/kg. It illustrates that the higher level of the three reagents (10 g/kg) decreases the selectivity of separation compared to the lower level (4 g/kg). The maximum selectivity index B at the 10 g/kg level was 0.278 corresponding to the dodecane:$C_{12}E_4$:pentanol ratio of 1:3:1. Other three-reagent combinations resulted in a relatively low values of selectivity index B ranging from 0.169 (at dodecane:$C_{12}E_4$: pentanol ratio of 1:1:1) to 0.275 (dodecane:$C_{12}E_4$: pentanol ratio of 2:2:1). In addition, 10 g/kg of the $C_{12}E_4$-pentanol two-reagent system resulted in the highest separation efficiency reaching 0.312 at the $C_{12}E_4$:pentanol ratio of 3:2.


a) selectivity index B response map

b) selectivity index B contour map

Fig. 53. Effect of dodecane-$C_{12}E_4$-pentanol combinations on coal selectivity at total dosage of 10 g/kg applying NCF/A. a) response map showing studied combinations and obtained results. Circles indicate studied points and values represent selectivity index B, b) contour map of selectivity index B drawn from data in Fig. 53a

Figure 53b shows the selectivity index B contour map based on data of Fig 53a. It illustrates widely spread contour lines having low values. They indicate that at a high dosage of the reagents the selectivity is not much sensitive to the change of reagents ratios. In general, the three-reagent combinations at both levels confirmed the better performance of the two-reagent system over the three-reagent one.

6.2.2. Flotation results using normal-contact flotation procedure (NCF) version B

It is clear that among the applied in one-, two-, and three-reagent systems using the NCF/A procedure, the two-reagent systems provided relatively best results but with low upgrading parameters values. Among the considered two-reagent systems, the most selective two-reagent systems were the $C_{12}E_4$-pentanol and the dodecane-$C_{12}E_4$ one. The dodecane-$C_{12}E_4$ system was selected for further investigation because of the usual application of hydrocarbons as collectors in coal flotation. It was used to test the coal flotation performance applying normal-contact flotation approach B (NCF/B), i.e. the two reagents were prepared together as a mixture in distilled water. Different dodecane-$C_{12}E_4$-water combinations were selected at a total dosage of dodecane+$C_{12}E_4$ of 10g/kg. They are shown in Table 20.

Table 20. Different combinations of dodecane-$C_{12}E_4$-water used for coal flotation at dodecane+$C_{12}E_4$ dosage of 10g/kg applying NCF/B procedure

Exp. # / Reagent	Reagent content, % (on weight basis)									
	1	2	3	4	5	6	7	8	9	10
Dodecane	30	60	5	35	60	20	10	22.5	35	25
Water	60	30	75	40	15	40	40	22.5	10	5
$C_{12}E_4$	10	10	20	25	25	40	50	55	55	70

Figure 54a shows the clean coal yield obtained with different studied combinations shown in Table 20, at a total dosage of $C_{12}E_4$+dodecane of 10 g/kg, together with results obtained using different concentrations of one-reagent in water. The maximum clean coal yield in this series was 64.5% having ash content 2.52%. It corresponds to the dosage of 3.9 and 6.1 g/kg dodecane and $C_{12}E_4$, respectively, reflecting the dodecane:$C_{12}E_4$ weight ratio of ~1:1.6. It is different from the 4:1 dodecane:$C_{12}E_4$ ratio required to achieve the maximum yield using the same system and applying the NCF/A procedure. This maybe attributed to interactions taking place between the coal particles and oil droplets as well as air bubbles with each other in water.

Figure 54b presents clean coal yield contour map drawn from Fig. 54a using the Surfer Version 7 software. The clean coal yield contours are crowded near the dodecane apex. This reflects the necessity of either good emulsification or use of frother as $C_{12}E_4$ to achieve flotation with dodecane. The contours near the borders are closed and crowded, while at the center they have wide gaps.

Figures 55 gives clean coal ash content and its contour map. Figure 55a shows that clean coal with the ash content ranging from 1.8-2.86% can be obtained from this series. It also indicates that using either $C_{12}E_4$ or dodecane alone in water can lead to a cleaner coal compared to mixing both reagents with water. Figure 55b shows the clean coal ash contour map. The contours are crowded at the outside corners but have significant gaps in the interior of the plot. The same trend can be noticed in the case of the clean coal yield.

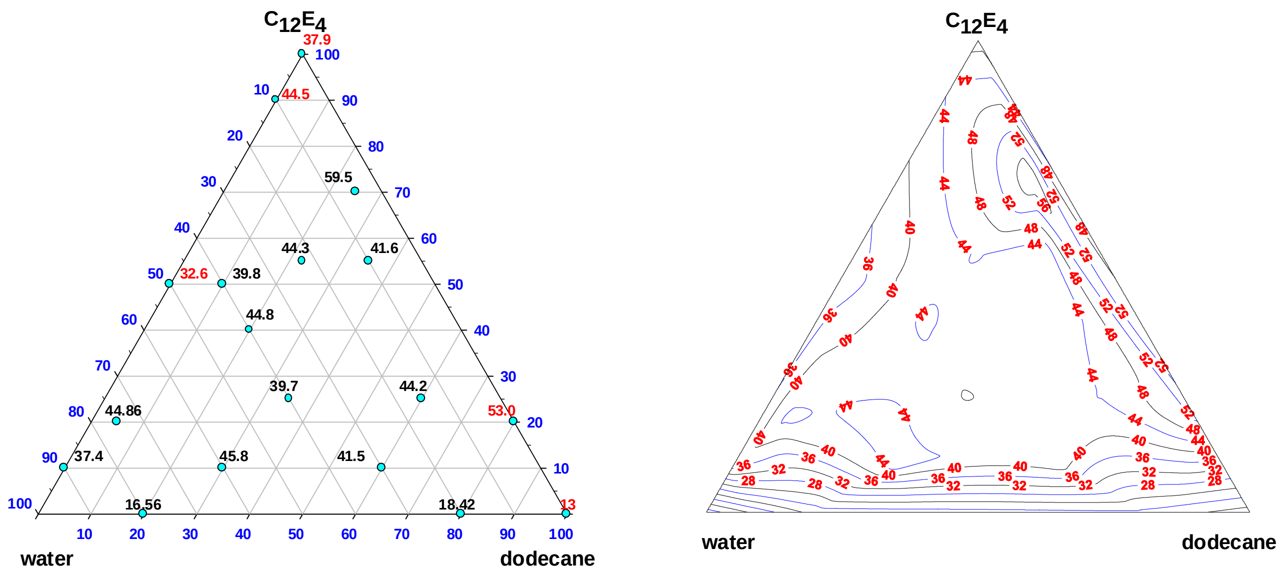

a) clean coal yield response map b) clean coal yield contour map

Fig. 54. Effect of different concentrations of water-dodecane-$C_{12}E_4$ system on clean coal yield at total dosage of 10 g/kg using NCF/B procedure, a) clean coal yield response map, b) clean coal yield contour map drawn from Fig. 54a

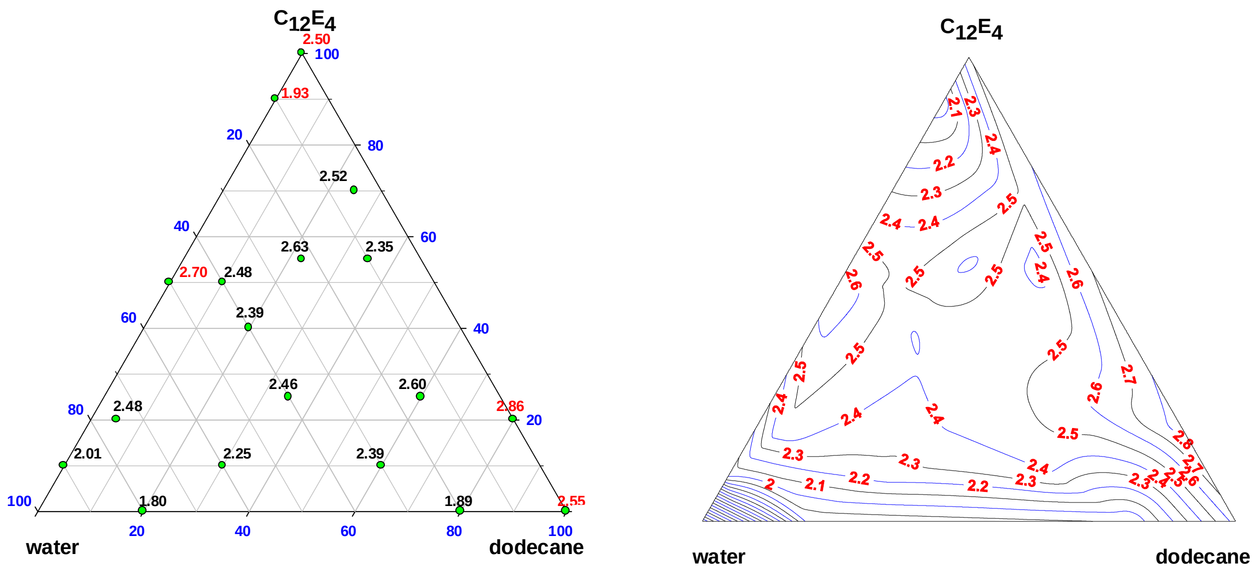
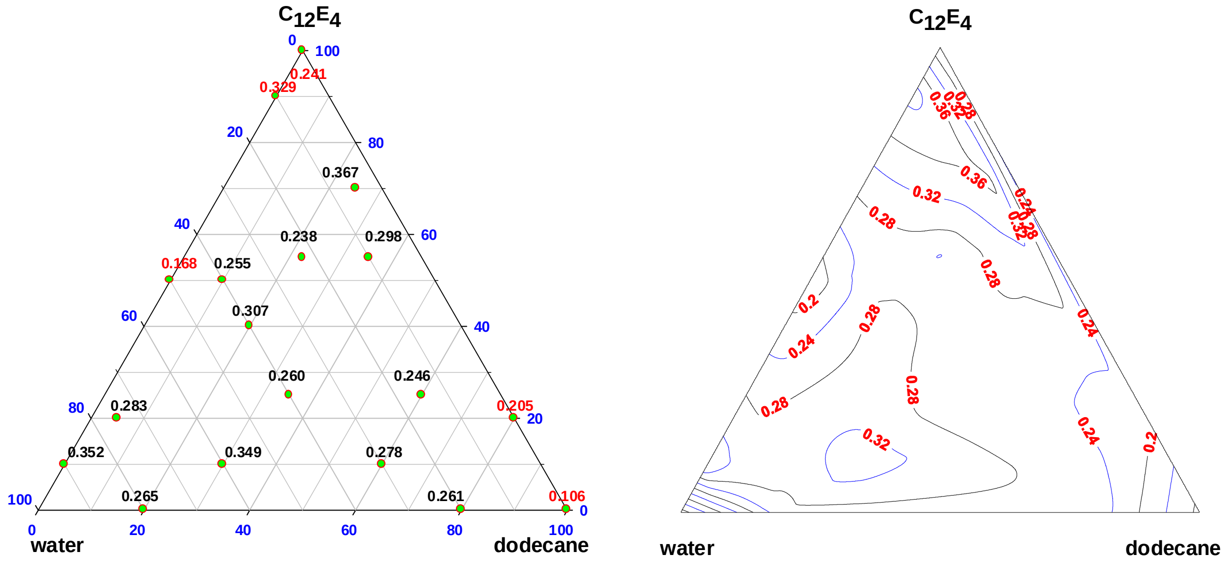

a) clean coal ash content response map b) clean coal ash contour map

Fig. 55. Effect of different concentrations of water-dodecane-$C_{12}E_4$ system on clean coal ash content at a total dosage of 10 g/kg using NCF/B procedure, a) clean coal ash content response map, b) clean coal ash contour map drawn from Fig. 55a

Figure 56 shows the results of combining the two parameters (yield and ash of clean coal) by considering selectivity index B.



a) response map of coal selectivity index B b) contour map of selectivity index B

Fig. 56. Effect of different concentrations of water-dodecane-$C_{12}E_4$ system on clean coal selectivity index B at total dosage of 10 g/kg using NCF/B procedure, a) selectivity index B response map, b) selectivity index B contour map based on data from Fig. 56a

Figure 56a shows that selectivity indices have a wide range in spite of using the same dosage at different concentrations of components. Figure 56b shows a selectivity contour map drawn from Fig. 56a. The contour lines have wide gaps and they are haphazardly distributed reflecting no rule for the selectivity improvement.

6.2.3. Evaluation of coal flotation results applying both normal-contact flotation procedures (NCF/A, NCF/B)

The detailed investigation regarding flotation of oxidized coal applying the normal-contact flotation procedure (NCF) reflected poor clean coal yield regardless of the number of reagents used and procedure type (version) which maybe attributed to coal surface hydration. The procedure also provided a low selectivity. It maybe explained in the light of physical and chemical interactions between coal particles leading to non-selective aggregation. The low clean coal yields coupled with the low selectivity showed that:

1- one-reagent system normal-contact flotation procedure (NCF/A) resulted in a maximum clean coal yield of less than 37% (with $C_{12}E_4$). Above a certain dosage of reagents under study (10 g/kg) there is no significant improvement in either yield or ash content of the clean coal. The maximum selectivity index B was 0.172 compared to its scale of 0 to 1

2- using different two-reagent systems applying the same (NCF/A) procedure at a constant dosage of 4g/kg with different ratios revealed co-existence of a positive synergetic effect. The extent of this synergetic effect depends on the type of the two reagents under investigation. Separation efficiencies obtained, when changing the two reagent dosage at their optimum ratio, was found to be also dependent on the type of the two reagents under study

3- using three reagents under different combinations at total dosage levels (4 and 10 g/kg) leads to the conclusion that two-reagent system is preferable from both the quantity and quality point of view

4- applying the other normal-flotation version (NCF/B) showed that this procedure increases clean yield for a given two-reagent system but drastically effects the quality of products.

Therefore it can be generally summed up that, the normal-contact flotation procedure using typical flotation reagents can not be used for upgrading the investigated here difficult-to-float oxidized coal because the process responses regarding the clean coal yield, ash content, and separation results are poor. Probably, the reason of that maybe the oxidized coal after the wetting step does not adsorb well the hydrophobization reagents. Therefore, in the next chapter another approach will be used in which the dry coal will be brought into contact directly with the anhydrous or highly concentrated reagents. This approach will be called the direct-contact flotation and should provide information about the potentials of flotational separation for a particular material, in this case the investigated oxidized coal.

6.3. Coal flotation applying direct-contact flotation procedure (DCF)

It appears from hitherto carried out experiments that the normal-contact flotation procedure suffers from low recovery of the investigated oxidized coal and lack of selectivity. It results from the hydrophilic nature of the coal surface enhancing its hydration after contact with water and hence preventing selective adsorption of reagents on its surface. These shortcomings can be appreciably addressed by selection of a completely different procedure designed in this thesis to avoid the negative effects encountered during the normal-contact flotation. For this reason, a special procedure, referred to as the direct-contact flotation procedure or DCF was applied.

Results regarding the application of the direct-contact flotation for upgrading oxidized coal will be discussed in this section of the thesis.

6.3.1. Flotation results using direct-contact flotation procedure (DCF) version A

6.3.1.1. DCF/A of coal in the presence of a single reagent

A series of tests was carried out applying the direct-contact flotation procedure (DCF/A) using a single-reagent scheme. From the six considered-in-this-work reagents, only $C_{16}E_{23}$ was not used in this series because it was solid at room temperature. The other different reagents (heptane, dodecane, $C_{12}E_4$, pentanol, and α-terpineol) were liquids at ambient temperature and were applied in an anhydrous form. Figure 57 depicts the clean coal yield and its ash content obtained with changing the dosage of each reagent using the DCF/A procedure. It shows that better flotation responses (especially clean coal yield) than those with the NCF/A procedure can be obtained. However, they are achieved at higher dosages of the reagents. Taking into account the dosage of 20 g/kg, the reagents were arranged according to the responses as shown in Eq. 19 (yield) and Eq. 20 (ash content). The considered responses are written in parentheses in %. The arrangements are given by the equations:

$$\textbf{heptane (0.0)} < \textbf{terpineol (20.6)} < \textbf{pentanol (27)} < \textbf{dodecane (\sim 41.5)} < \mathbf{C_{12}E_4}\ \textbf{(\sim 50)}$$

$$\text{(Effect of one-reagent dosage on clean coal yield at 20 g/kg)} \qquad (19)$$

terpineol (2.95)>pentanol (2.89)>dodecane (2.63)>$C_{12}E_4$ (2.23)

(Effect of one-reagent dosage on clean coal ash content at 20 g/kg) (20)

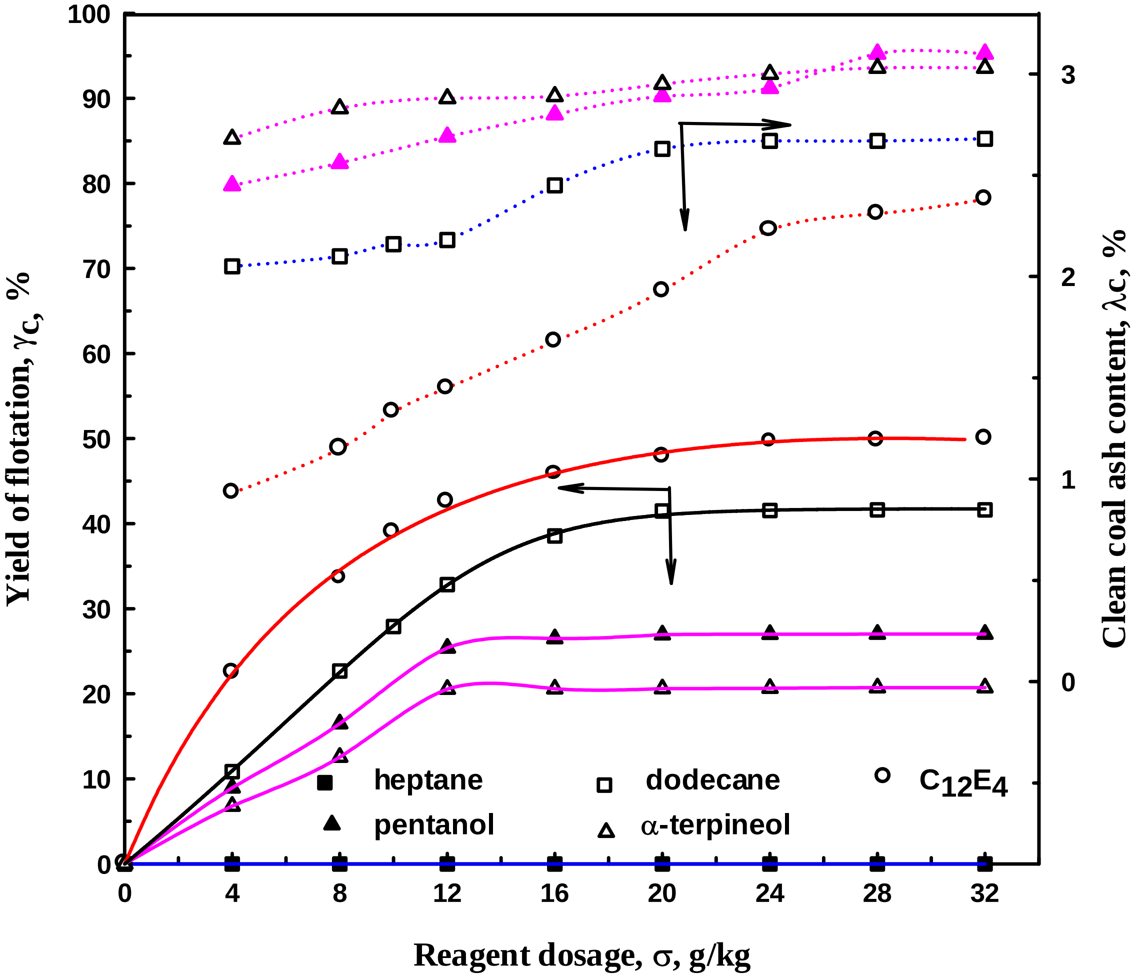


Fig. 57. Effect of one-reagent (its type and dosage) on flotation yield of clean coal and clean coal ash content applying direct-contact flotation (DCF/A) procedure. Each point represents a separate test

The results show that nonionic surfactants ($C_{12}E_4$) can lead to an improvement in both quality and quantity when applied using the DCF/A procedure. This agrees with the fact that incorporating certain functional groups or atoms into surfactant molecules may have a dramatic impact on the surface activity of the chemicals (Harris and Jia, 2000). The data illustrated also that alcohols may have collecting power when they are directly mixed with dry coal leading to higher clean coal yields. It should be noticed that increasing the reagent dosage above 20 g/kg did not have any improvement on either clean coal yield or its ash content.

Figure 58 represents the Fuerstenau plot with selectivity encountered for this series. It should be stressed that all the investigated dosages of each reagent were approximated with Eq. 2B as a series leading to single selectivity index B for each reagent. Also the statistical measure (R^2) was of low values compared to normal flotation results fitting. The different used reagents can be arranged on the selectivity index B (given in parenthesis) as follows:

terpineol (0.066)<pentanol (0.093)<dodecane (0.227)<$C_{12}E_4$ (0.445)

(Effect of one-reagent dosage on selectivity index B) (21)

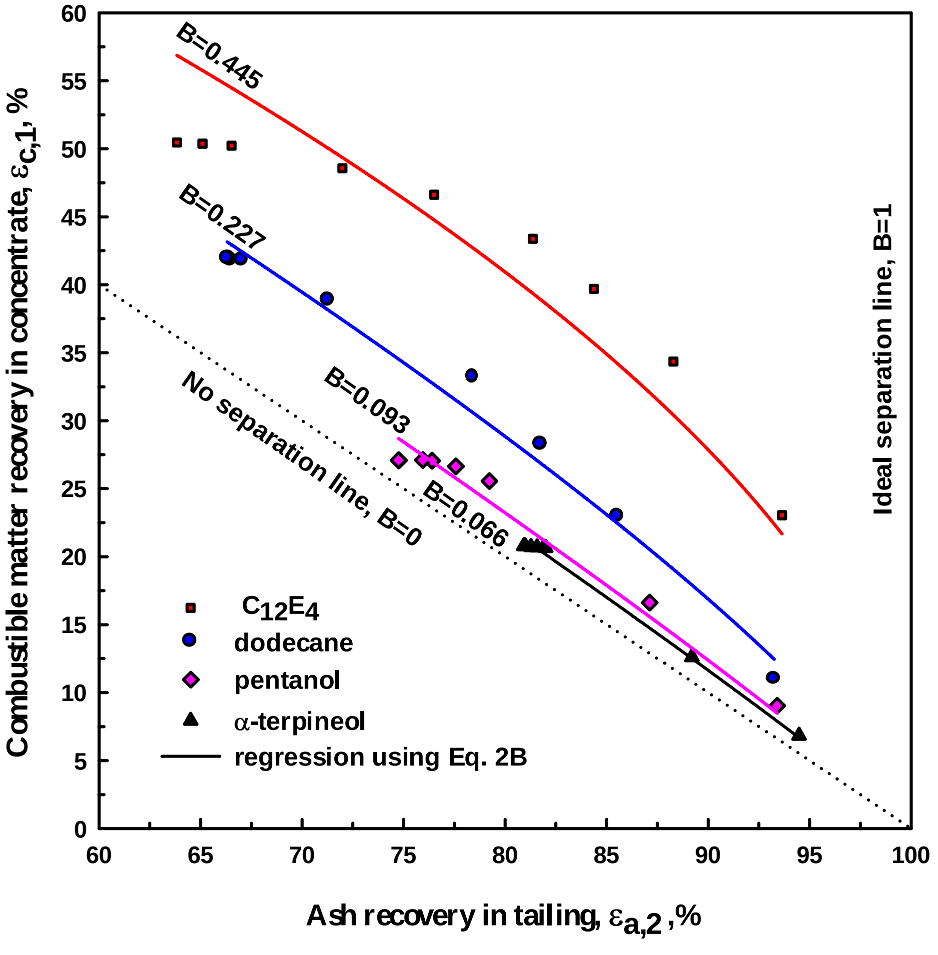


Fig. 58. Fuerstenau's plot showing effect of reagent, type and dosage, on separation of coal using direct-contact flotation DCF/A procedure. Based on results of Fig. 57

Figure 59 shows a comparison of different reagents concerning their separation efficiency index B in the case of direct-contact (DCF/A) and normal-contact (NCF/A) flotation procedures. The separation efficiency applying the DCF/A procedure is higher than that encountered in the case of the NCF/A flotation procedure. The highest difference was noticed for $C_{12}E_4$. The reason for the lack of selectivity for both procedures when using hydrocarbons or alcohols could be explained by their non-selective adsorption on both coal and ash-forming matter (Aplan, 1993) and by the entrapment of ash in the coal agglomerates readily formed by the bridging action of the oily collectors as discussed by Chander et al. (1996).

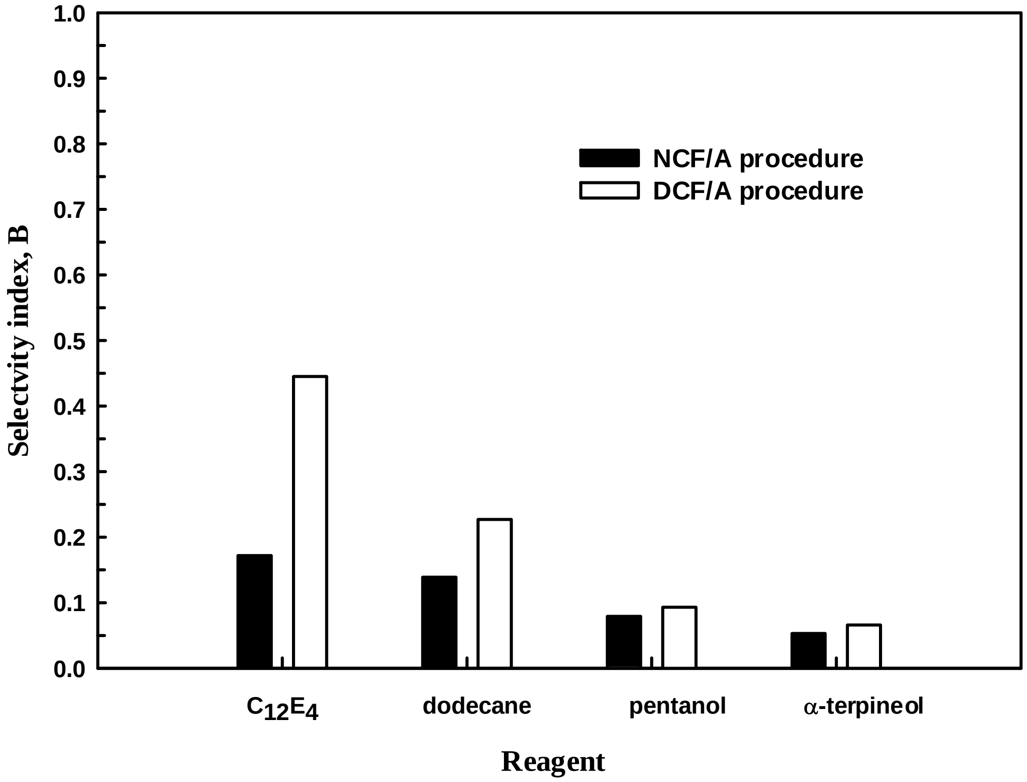


Fig. 59. Separation efficiency indices using one-reagent system applying NCF/A and DCF/A flotation procedures.

It can be concluded that applying the direct-contact flotation DCF/A procedure in the one-reagent scheme for upgrading the investigated difficult-to-float oxidized coal leads to an improvement of the clean coal yield, its ash content, and also the overall process selectivity.

6.3.1.2. DCF/A of coal in the presence of two reagents

Based on the results obtained from the single-reagent series using the direct-contact DCF/A procedure, two-reagent systems, representing different combinations and concentrations, were investigated. The studied two-reagent systems were selected from the previous systems considered for the normal-contact flotation (NCF) procedure. From the first two-reagent hydrocarbon-alcohol series, only heptane-pentanol, and dodecane-pentanol systems were considered. This is because pentanol was better than α-terpineol. From the second series, hydrocarbons mixed with alkyl poly(ethylene glycol) ethers (C_xE_y), only heptane-$C_{12}E_4$, and dodecane-$C_{12}E_4$ were used because $C_{16}E_{23}$ was solid at room temperature in addition to its poor results reported during the normal-contact flotation procedure. The third and last series of the two-reagent direct-contact flotation procedure was based on mixing alkyl poly(ethylene glycol) ethers (C_xE_y) with alcohols and only the $C_{12}E_4$-pentanol two-reagent system was investigated.

The two reagents ratio in each system was first investigated at a total dosage of the two reagents together equal to 8 g/kg. Figure 60(a-c) shows the clean coal yield for various ratios of the two reagents. Figure 60a shows a synergetic effect at the alcohol/hydrocarbon ratio of 1:4. The optimum C_xE_y/hydrocarbon ratio was also 1:4 (Fig. 60b). On the other hand, the best alcohol/C_xE_y ratio was found to be at 2:3 (Fig. 60c). The clean coal yields and their ash contents, obtained at the optimum ratio between the two reagents, have two different arrangements of all of the considered two-reagent systems in the three series. Equation 22 gives the arrangement based on the clean coal yield (given in parenthesis, %):

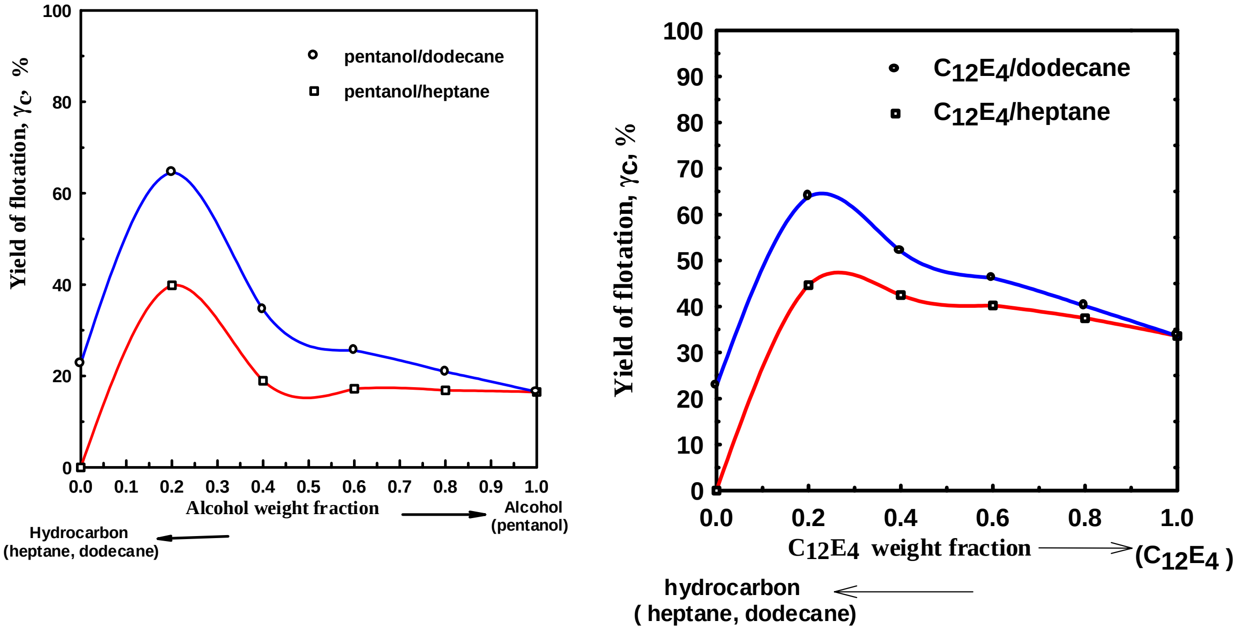
$$\frac{\textbf{heptane}}{\textbf{pentanol}}(\mathbf{39.9}) < \frac{\textbf{heptane}}{\mathbf{C_{12}E_4}}(\mathbf{44.7}) < \frac{\textbf{dodecane}}{\mathbf{C_{12}E_4}}(\mathbf{63.9}) < \frac{\textbf{dodecane}}{\textbf{pentanol}}(\mathbf{64.6}) < \frac{\mathbf{C_{12}E_4}}{\textbf{pentanol}}(\mathbf{69.9})$$

(Effect of two reagents ratio on clean coal yield at constant dosage of 8g/kg) (22)

The series order based on the ash content of clean coal is given in Eq. 23 (clean coal ash content is given in parenthesis, %).

$$\frac{\textbf{heptane}}{\textbf{pentanol}}(\mathbf{2.88}) > \frac{\textbf{heptane}}{\mathbf{C_{12}E_4}}(\mathbf{2.76}) > \frac{\textbf{dodecane}}{\textbf{pentanol}}(\mathbf{2.33}) > \frac{\mathbf{C_{12}E_4}}{\textbf{pentanol}}(\mathbf{2.3}) > \frac{\textbf{dodecane}}{\mathbf{C_{12}E_4}}(\mathbf{2.18})$$

(Effect of two reagents ratio on clean coal ash content at constant dosage of 8g/kg) (23)


a) alcohol/hydrocarbon ratio at 8g/kg

b) C_xE_y/hydrocarbon ratio at 8g/kg

c) alcohol/C_xE_y ratio at 8g/kg

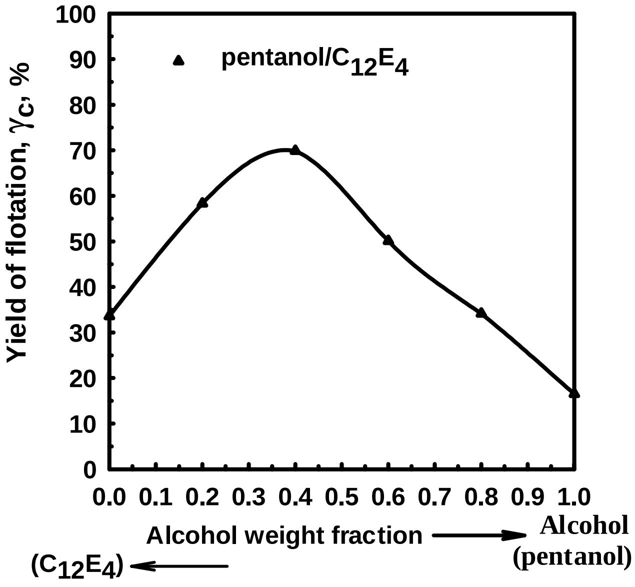
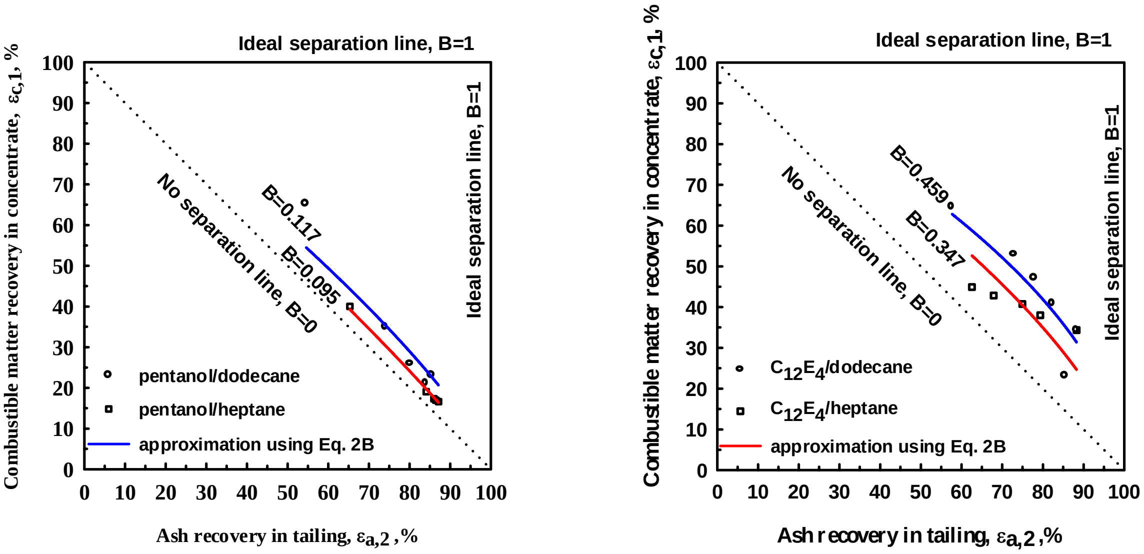


Fig. 60. Effect of two reagents ratio on clean coal yield at total dosage of 8 g/kg applying direct-contact flotation procedure (DCF/A), a) alcohol/hydrocarbon, b) C_xE_y/hydrocarbon, and c) alcohol/C_xE_y

Figure 61(a-c) shows the Fuerstenau plot illustrating coal upgrading resulted from changing the different ratios of the two reagents at a constant dosage (8g/kg). The obtained results provided the following values of the selectivity index B (given in parenthesis).

$$\frac{\textbf{heptane}}{\textbf{pentanol}}(0.095)<\frac{\textbf{dodecane}}{\textbf{pentanol}}(0.117)<\frac{\textbf{heptane}}{C_{12}E_4}(0.347)<\frac{C_{12}E_4}{\textbf{pentanol}}(0.409)<\frac{\textbf{dodecane}}{C_{12}E_4}(0.459)$$

(Effect of two reagents ratio on selectivity index B at constant dosage of 8g/kg) (24)


a) alcohol/hydrocarbon ratio at 8g/kg

b) C_xE_y/hydrocarbon ratio at 8g/kg

c) alcohol/C_xE_y ratio at 8g/kg

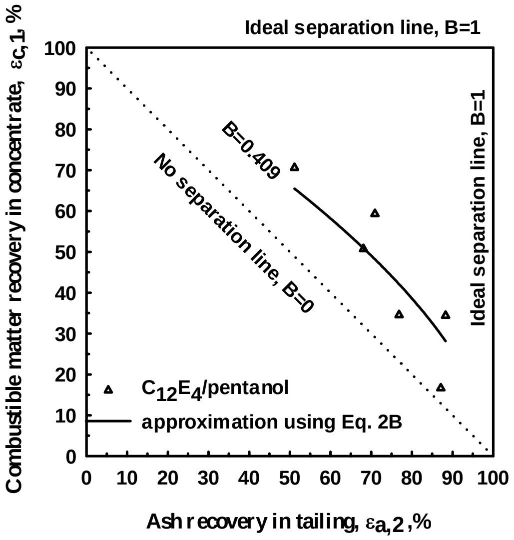


Fig. 61. Furestenau's plot showing the effect of two reagents ratio on separation of coal at constant dosage of 8 g/kg applying direct-contact flotation procedure (DCF/A). a) alcohol/hydrocarbon, b) C_xE_y/hydrocarbon, and c) alcohol/C_xE_y. Based on results of Fig. 60

Figure 62 shows a comparison of the two-reagent systems when the ratio between the two reagents was changed applying both the direct-contact flotation (DCF/A) and normal-contact flotation (NCF/A) procedures. It indicates that the direct-contact flotation is better than normal-contact flotation for majority of the considered systems. It is clear that selectivity index B obtained with different ratios of the two reagents using the NCF/A procedure (at the total reagents dosage of 4g/kg) is lower than that obtained applying the DCF/A procedure (at the total reagents dosage of 8g/kg) (except the dodecane-pentanol system). The studied systems have the same arrangement order regarding their separation efficiency for both procedures but with different values of the separation efficiency index. The maximum separation efficiency was achieved in both cases when mixing dodecane with $C_{12}E_4$ because the selectivity index B was 0.253 and 0.459 for normal- and direct-contact flotation procedures, respectively. Therefore, the best two-reagent system is dodecane-$C_{12}E_4$ applied with the direct-contact flotation procedure having separation index B equal to 0.459.

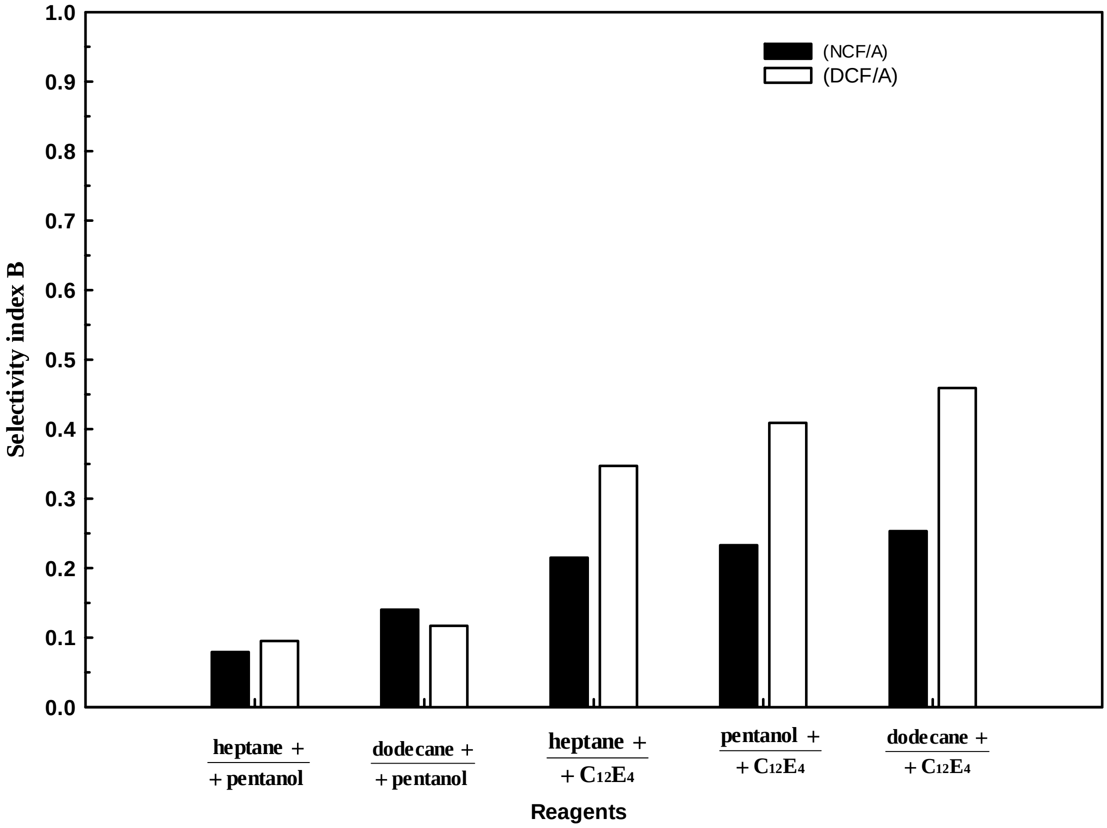


Fig. 62. Effect of reagents ratio on separation efficiency index B obtained by applying normal-contact flotation (NCF/A) procedure at 4 g/kg and direct-contact flotation (DCF/A) procedure at 8 g/kg

Figure 63 shows the clean coal yield obtained when changing the total dosage of hydrocarbons and pentanol at an optimum predetermined alcohol/hydrocarbon ratio of 1:4. It shows that there exists a high improvement when increasing the total dosage of the two-reagents. At a total dosage of 20 g/kg of the heptane-pentanol system, a clean coal yield of ~81 % with 3.12% ash was obtained. In the case of the dodecane and pentanol two-reagent system at the same dosage of 20 g/kg, a clean coal yield of 94.5% having 2.62% ash was produced. Application of a higher dosage of the two reagents improves neither clean coal yield nor its ash content in the heptane-pentanol system. For the dodecane-pentanol system, a slight improvement in the clean coal yield required a moderately higher dosage of the two reagents. Then, a maximum clean coal yield of about 98.5% having ash 3.12% was obtained at a total dosage of 30 g/kg.

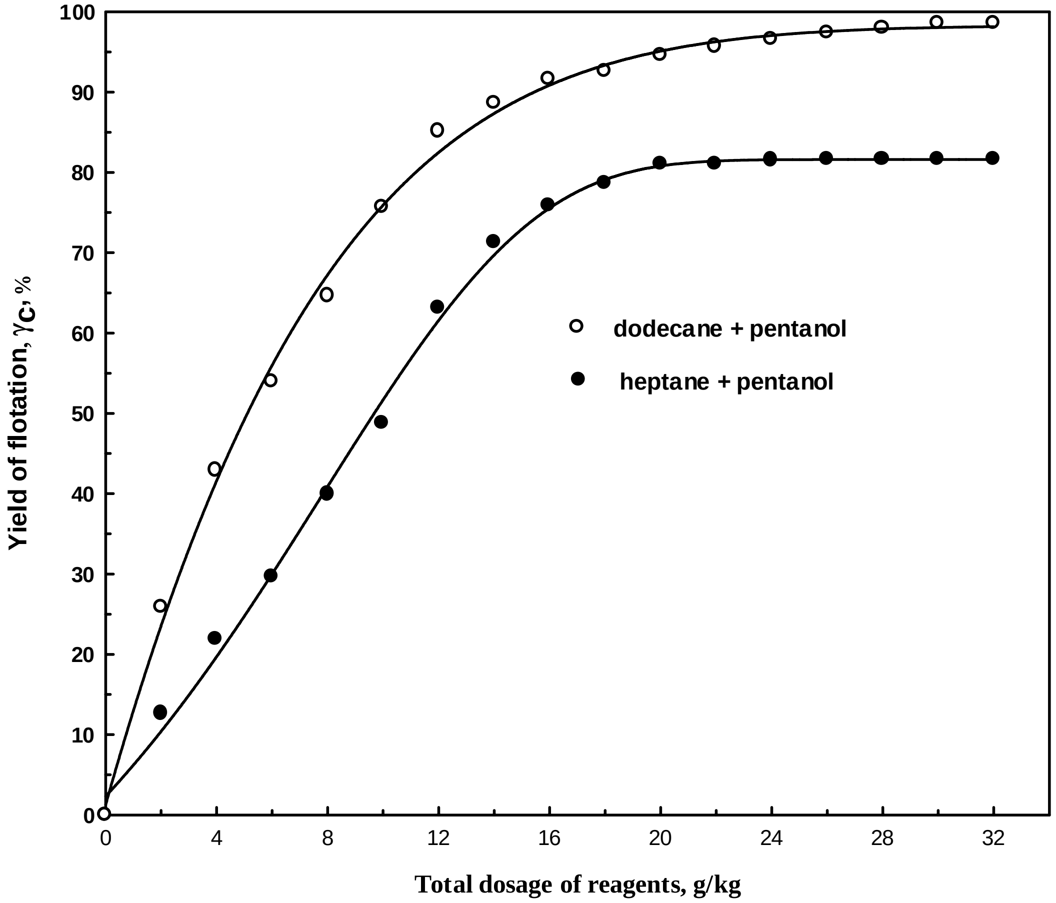


Fig. 63. Effect of hydrocarbon+alcohol (type and dosage) on the clean coal yield at optimum alcohol/hydrocarbon ratio of 1:4 applying DCF/A procedure

Figure 64 shows the Fuerstenau plot illustrating separation encountered in this series. It is clear that the dodecane-pentanol system is better than the heptane-pentanol system regarding their separation efficiency index B corresponding to values of 0.471 and 0.155, respectively.

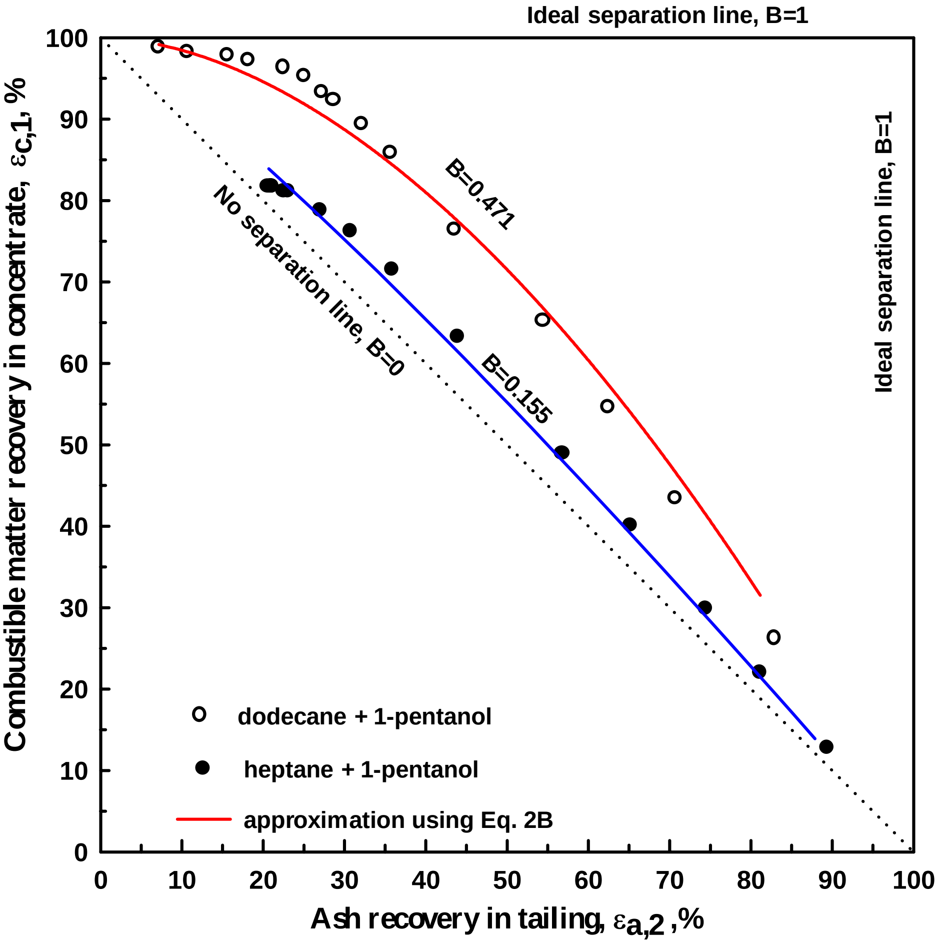


Fig. 64. Fuerstenau's plot showing effect of alcohol+hydrocarbon dosage on coal separation at alcohol/hydrocarbon ratio of 1:4 applying DCF/A procedure. Based on results of Fig. 63

Figure 65 illustrates the effect of total dosage of hydrocarbons+$C_{12}E_4$ two-reagent systems on the clean coal yield at an optimum $C_{12}E_4$/hydrocarbons ratio of 1:4. It shows an excellent flotation response. At the total dosage of 20 g/kg of dodecane+$C_{12}E_4$, a clean coal yield of 92.56% containing 2.22 % ash was obtained. The clean coal yields of 41.5 % (2.63% ash) and 47.89% (1.93% ash) were obtained for dodecane and $C_{12}E_4$ at the same dosage, when each of them was used alone under the same direct-contact procedure. The heptane+$C_{12}E_4$ system at this dosage (20 g/kg) resulted in a clean coal yield reaching 82.6% and containing 2.93 % ash, which has not been achieved before for this system.

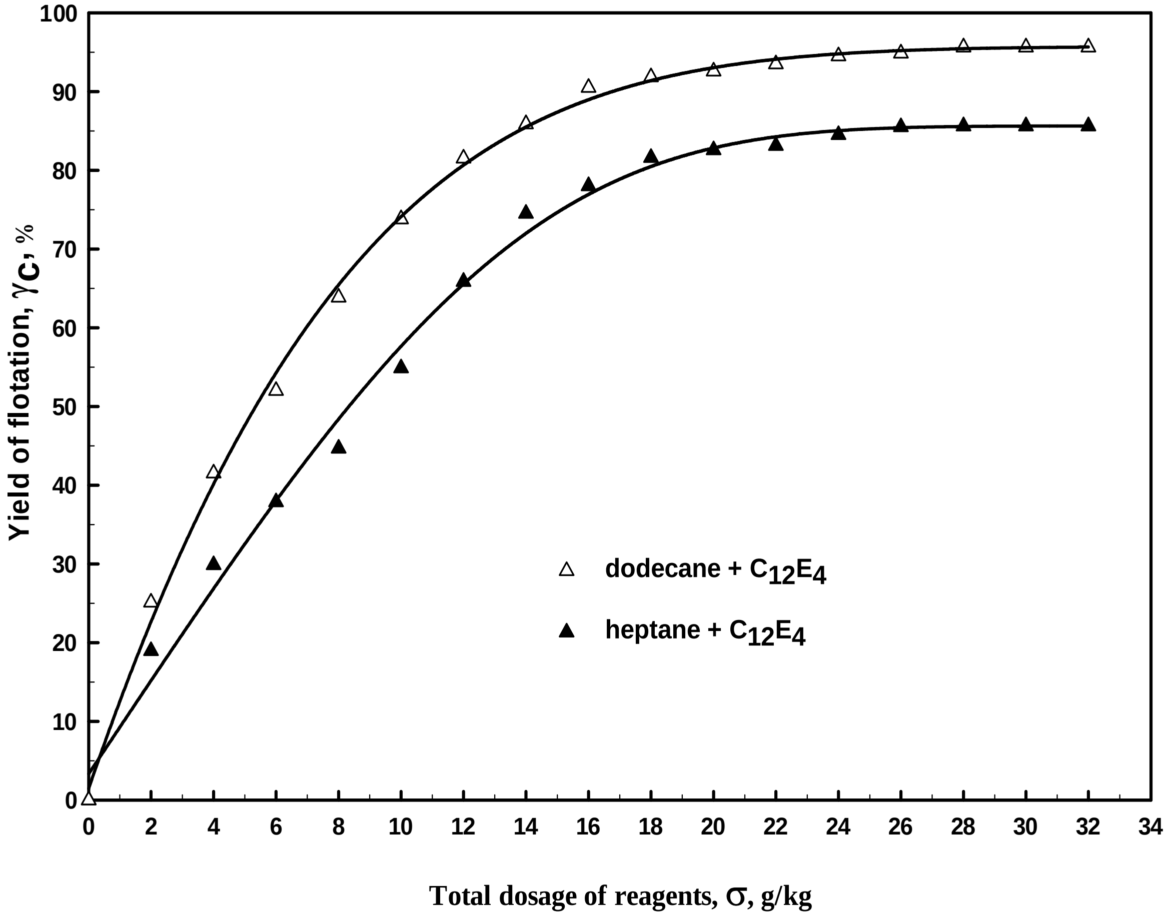


Fig. 65. Effect of $C_{12}E_4$+hydrocarbon (type and dosage) on clean coal yield at an optimum $C_{12}E_4$/hydrocarbon of 1:4 applying DCF/A procedure

Figure 66 shows the Fuerstenau plot illustrating separation in the $C_{12}E_4$+hydrocarbon system regarding the clean coal yield at the optimum $C_{12}E_4$/hydrocarbon ratio of 1:4 applying the DCF/A procedure. It shows that the dodecane+$C_{12}E_4$ system resulted in a better separation compared with the heptane+$C_{12}E_4$ system corresponding to selectivity index B of 0.588 and 0.262, respectively. The trend of results agrees with that obtained in the case of applying the normal-contact flotation procedure for the same two-reagent systems with higher values of selectivity index B in the case of the DCF/A procedure.

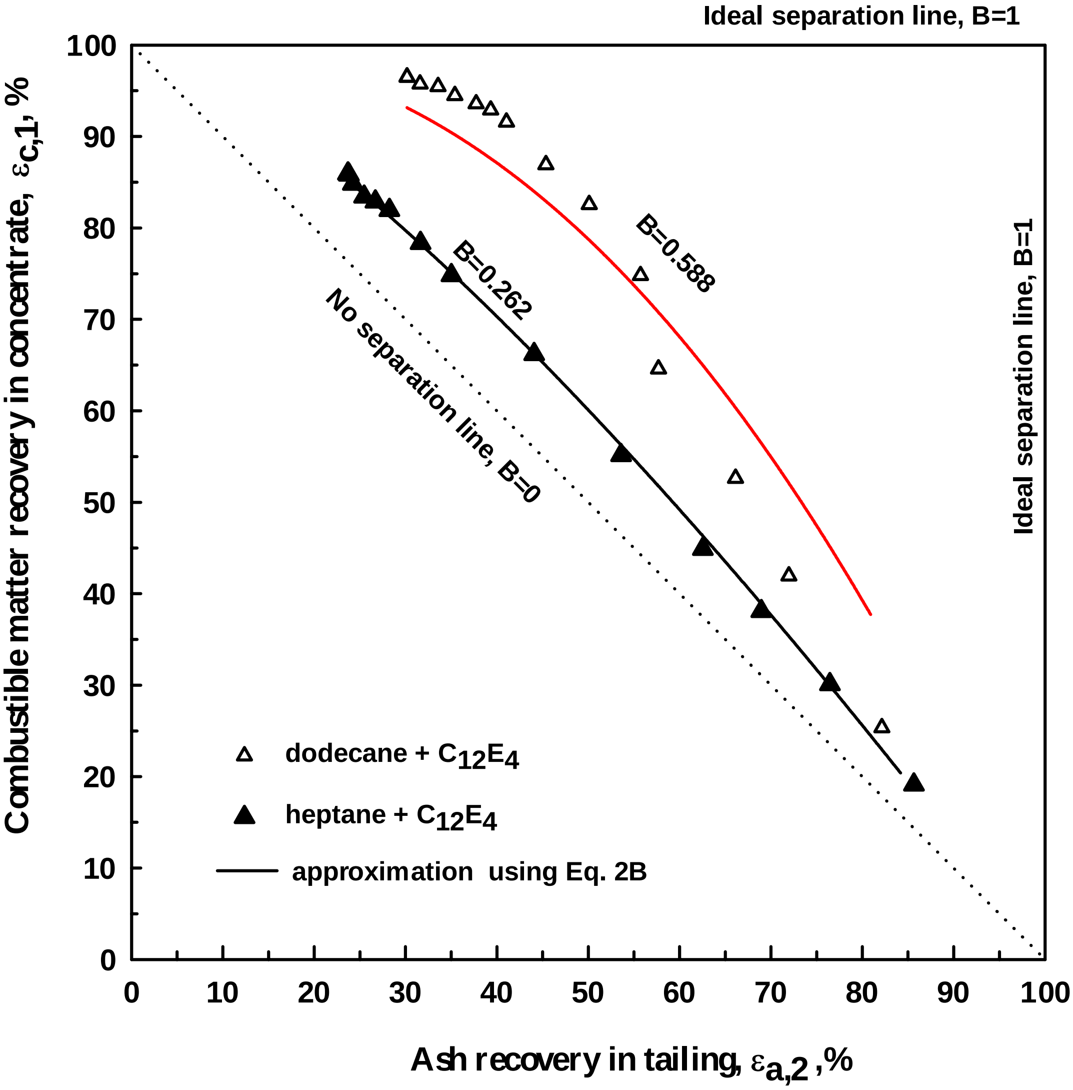


Fig. 66. Fuerstenau's plot showing effect of $C_{12}E_4$+hydrocarbon dosage on separation of coal using direct-contact flotation DCF/A procedure. Based on results of Fig. 65

Figure 67 gives the effect of the total dosage of the $C_{12}E_4$+pentanol mixture, which represents alkyl poly(ethylene glycol) ethers (C_xE_y) combined with alcohols, on the clean coal yield obtained at the optimum pre-determined ratio. At the total dosage of 20 g/kg of $C_{12}E_4$+pentanol, a clean coal yield of 94.5% containing 2.86 % ash was obtained in comparison with 26.95% (2.89% ash) and 47.89% (1.93% ash) yields for pentanol and $C_{12}E_4$ at the same dosage, when each of them is used alone, applying the direct-contact flotation DCF/A procedure.

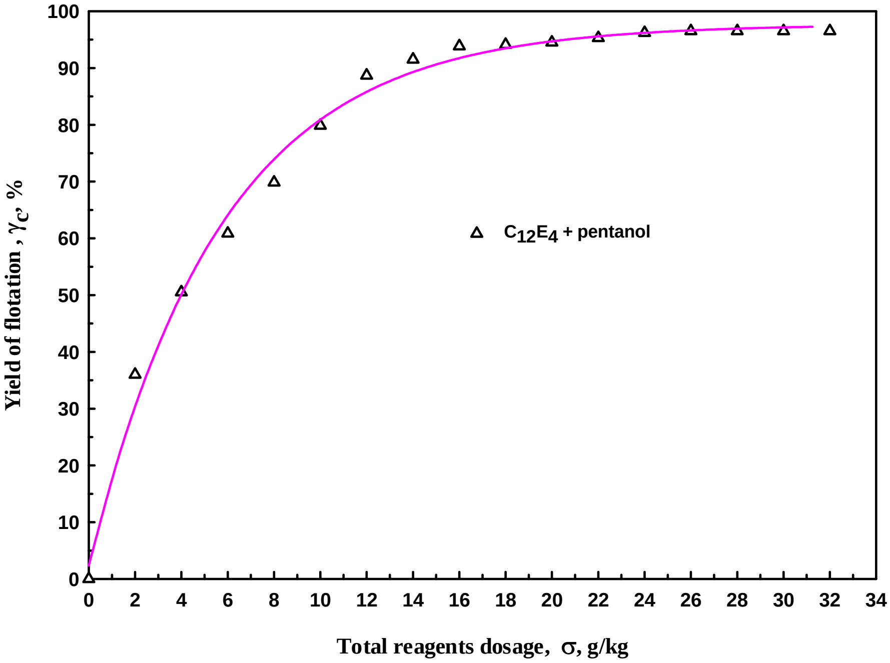


Fig. 67. Effect of $C_{12}E_4$+alcohol dosage on clean coal yield at an optimum alcohol/$C_{12}E_4$ ratio of 2:3 using direct-contact DCF/A procedure

Figure 68 shows the Fuerstenau separation plot for this two-reagent system. Selectivity index B for this system was equal to 0.480.

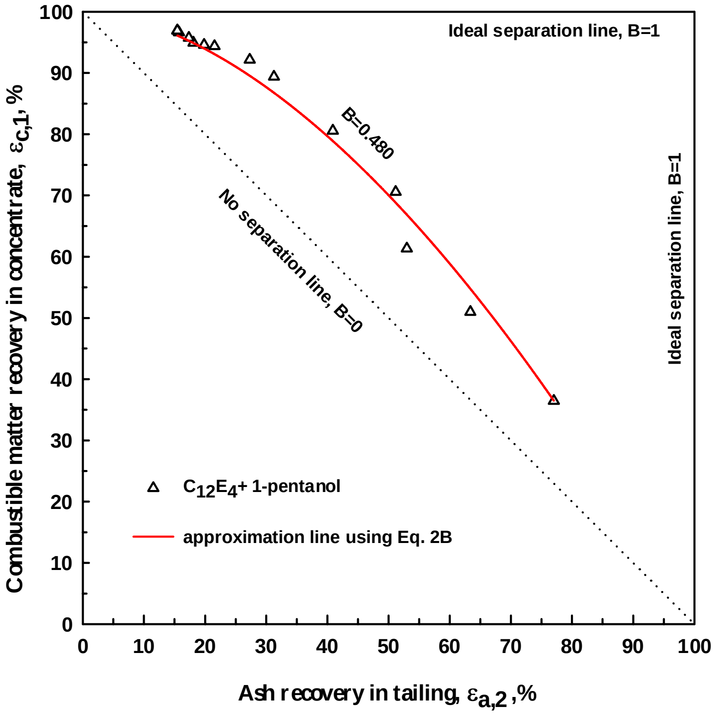


Fig. 68. Fuerstenau's plot showing effect of $C_{12}E_4$+alcohol dosage on separation of coal at optimum alcohol/$C_{12}E_4$ ratio of 2:3 using DCF/A procedure. Based on results of Fig. 67

Figure 69 represents separation efficiency index B obtained with different two-reagent dosages using the normal- and direct-contact flotation procedures at the optimum predetermined ratios.

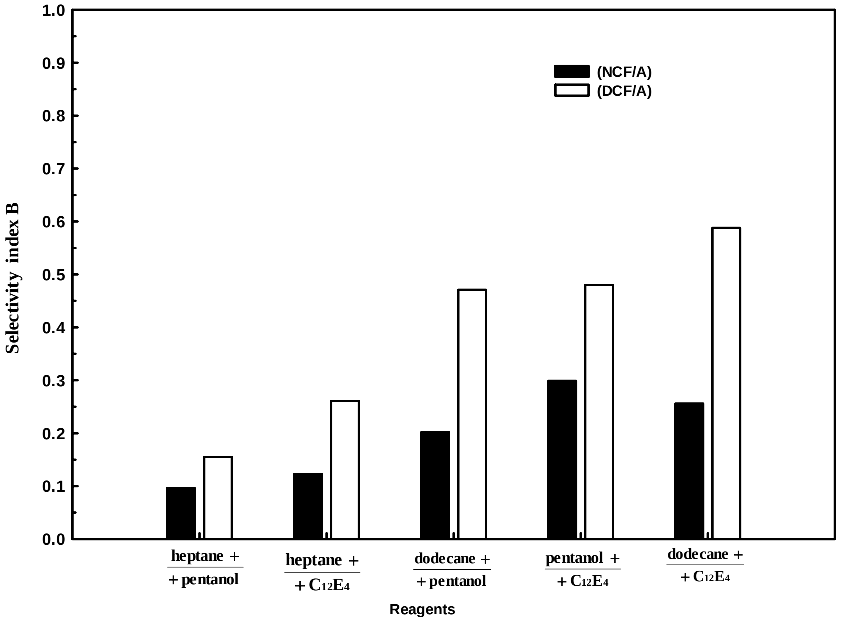


Fig. 69. Effect of two-reagent dosage on selectivity index B (approximation was run for all investigated dosages as a series) obtained applying both NCF/A and DCF/A flotation procedures

The studied systems have higher separation efficiency index B using the direct-contact flotation procedure. The systems arrangement, in the case of the normal-contact flotation NCF/A procedure, was as follows (B values in parenthesis):

$$\frac{\textbf{heptane +}}{\textbf{+ pentanol}}\textbf{(0.096)} < \frac{\textbf{heptane +}}{\textbf{+ C}_{\textbf{12}}\textbf{E}_{\textbf{4}}}\textbf{(0.123)} < \frac{\textbf{dodecane +}}{\textbf{+ pentanol}}\textbf{(0.202)} < \frac{\textbf{dodecane +}}{\textbf{+ C}_{\textbf{12}}\textbf{E}_{\textbf{4}}}\textbf{(0.256)} < \frac{\textbf{pentanol}}{\textbf{+ C}_{\textbf{12}}\textbf{E}_{\textbf{4}}}(0.299)$$

(Effect of two reagents dosage applying NCF/A procedure) (25)

While the systems arrangement in case of the direct-contact flotation DCF/A procedure was (B in parenthesis):

$$\frac{\textbf{heptane +}}{\textbf{+ pentanol}}\textbf{(0.155)} < \frac{\textbf{heptane +}}{\textbf{+ C}_{\textbf{12}}\textbf{E}_{\textbf{4}}}\textbf{(0.262)} < \frac{\textbf{dodecane +}}{\textbf{+ pentanol}}\textbf{(0.471)} \sim= \frac{\textbf{pentanol}}{\textbf{+ C}_{\textbf{12}}\textbf{E}_{\textbf{4}}}\textbf{(0.480)} < \frac{\textbf{dodecane +}}{\textbf{+ C}_{\textbf{12}}\textbf{E}_{\textbf{4}}}\textbf{(0.588)}$$

(Effect of two reagents dosage applying DCF/A procedure) (26)

It can be noticed that the system selectivity depends on the applied procedure, and the direct-contact flotation procedure DCF/A, as a rule, gives higher selectivity.

6.3.1.3. DCF/A of coal in the presence of three reagents

One- and two-reagent systems, applying the direct-contact flotation procedure, showed a great improvement in the coal flotation responses over the normal-contact flotation method. Therefore, a three-reagent dodecane-$C_{12}E_4$-pentanol system was investigated applying the DCF/A procedure. The different investigated three reagent combinations are shown in Table 21. The reagents were added in an anhydrous form. In the subsequent addition of reagents, the $C_{12}E_4$ required dosage was added first, followed by the needed dosage of dodecane, and finally, the necessary pentanol dosage was added. The different three-reagent combinations were applied at two different levels of their total dosage, that is 8 and 16 g/kg. The selected levels for investigation were just below the optimal effective reagent dosage in both procedures, that is (10 g/kg) for normal-contact and (20 g/kg) direct-contact flotation.

Table 21. Different dodecane-$C_{12}E_4$-pentanol ratios selected for coal flotation as three-reagent system applying direct contact-flotation procedure (DCF/A)

Exp. # / Reagent	wt. % in the seven considered combinations [Each reagent taken from pure (anhydrous) stock]						
	1	2	3	4	5	6	7
dodecane	60	40	20	33	40	20	20
$C_{12}E_4$	20	40	60	33	20	40	20
pentanol	20	20	20	34	40	40	60

Figure 70 illustrates the clean coal yield and its contour map at the lower dosage of the three reagents (8 g/kg) along with the results obtained for one- and two-reagent systems. Figure 70a shows that the maximum clean coal yield obtained for the different combinations of the three reagents is approximately 58.5 %. It was achieved twice, that is at the dodecane:$C_{12}E_4$:pentanol ratios of 3:1:1 and 1:2:2. At the same time, better clean coal yields were achieved using two-reagent systems at the same dosage (63.9% dodecane-$C_{12}E_4$, 64.6% dodecane-pentanol, and 69.9% $C_{12}E_4$-pentanol). Figure 70b shows the clean coal yield contour map drawn from Fig. 70a using the Surfer V.7 software. It shows parallel contours having low values near the plot apexes, increasing in the direction of the two- and three-reagent combinations. They were found to be also crowded near the apexes. It reflects the sensitivity of the clean coal yield to the reagent modification.

a) clean coal yield response map b) clean coal yield contour map

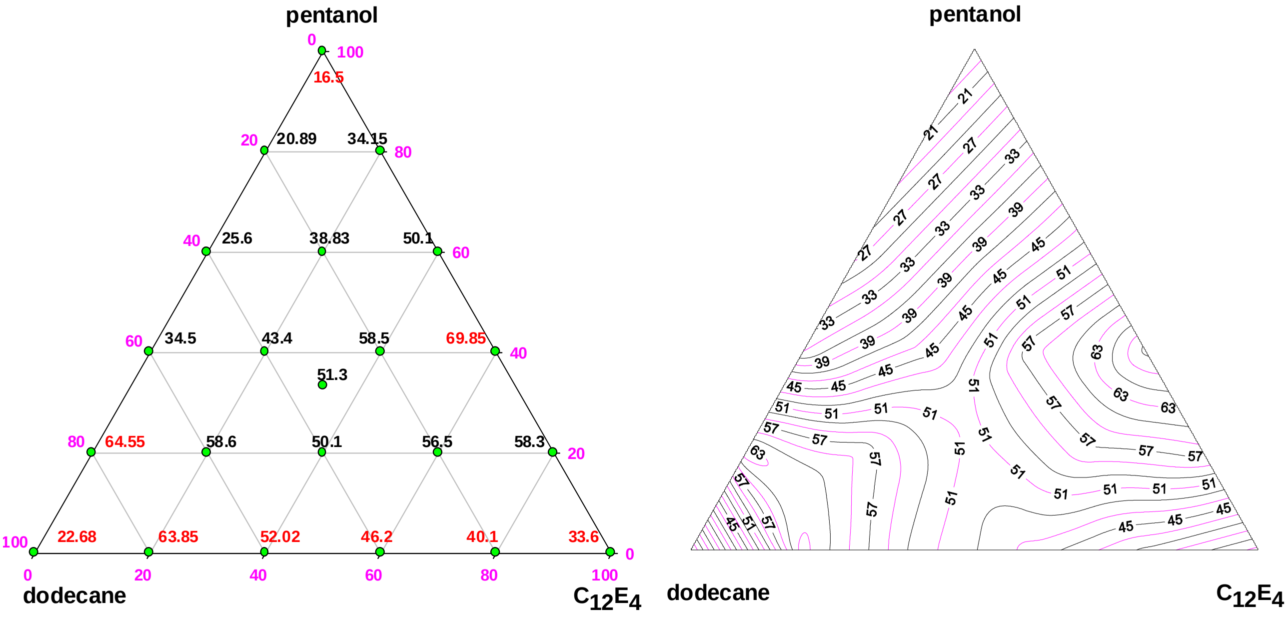
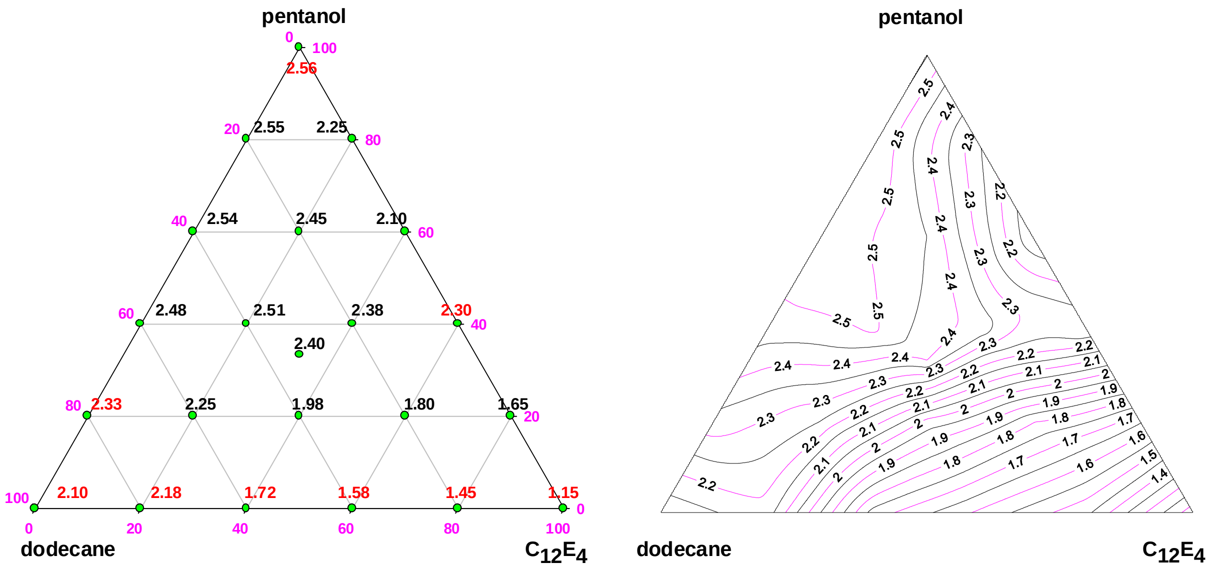


Fig. 70. Effect of different dodecane-$C_{12}E_4$-pentanol combinations on clean coal yield at total dosage of 8 g/kg applying DCF/A procedure. Ratios between the three-reagents are the same as read from the plot. a) response map studied combinations and obtained results. Circles indicate studied points and values represent clean coal yield in %, b) clean coal yield contour map based on data of Fig. 70a

Figure 71a-b depicts the clean coal ash content as response and contour maps obtained applying the different three-reagent combinations together with the results from one- and two-reagent systems at the total dosage of 8 g/kg. From Fig. 71a, it can be seen that the cleanest product, resulted from applying different three-reagent combinations, has an ash content of 1.8% at the dodecane:$C_{12}E_4$:pentanol ratio of 1:3:1. This does not correspond to the highest clean coal yield previously shown (Fig.

70a). It also shows that cleaner coal products can be obtained applying two-reagent systems or even one-reagent systems. For example, products having 1.45, 1.58, and 1.72% ash were obtained using different dodecane:$C_{12}E_4$ ratios as a two-reagent system while a product having ash content of 1.65 was obtained using the $C_{12}E_4$:pentanol ratio of 1:4. Meanwhile $C_{12}E_4$, as a one-reagent system, provided a product having the ash content of 1.15%.

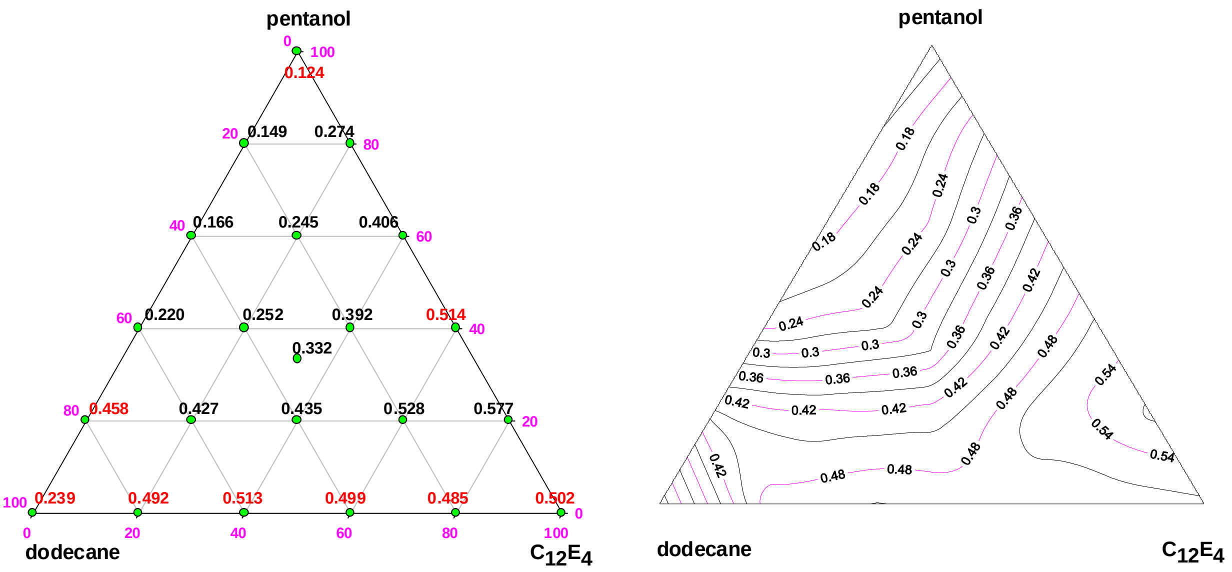

a) clean coal ash content response map

b) clean coal ash contour map

Fig. 71. Effect of dodecane-$C_{12}E_4$-pentanol combinations on clean coal ash at total dosage of 8 g/kg applying DCF/A procedure. Ratios among the three reagents are the same as read from plot. a) response map for studied combinations and obtained results. Circles indicate studied points and values represent clean coal ash content in %, b) clean coal ash contour map based on data from Fig. 71a

Figure 71b shows that clean coal ash contours are completely different from those obtained in the case of the normal-contact flotation NCF/A procedure, which reflects different adsorption mechanisms. These contours form two clear regions. The first is characterized by the low level of pentanol having crowded parallel contours extended horizontally with small inclination, while the second region has vertically extended contours at a higher level of pentanol. This shows that the high pentanol levels did not have a great effect on the clean coal ash content.

Figure 72a-b presents selectivity of separation resulted from the above series. Figure 72a indicates that the best three-reagent combination leads to selectivity index B of 0.528 corresponding to the dodecane:$C_{12}E_4$:pentanol ratio of 1:3:1. It also confirms the preference of the two-reagent over three-reagent systems, where selectivity index B of 0.577 was obtained using the pentanol:$C_{12}E_4$ ratio of 1:4 and 0.513 for dodecane:$C_{12}E_4$ ratio of 2:3.


a) selectivity index B response map

b) selectivity index B contour map

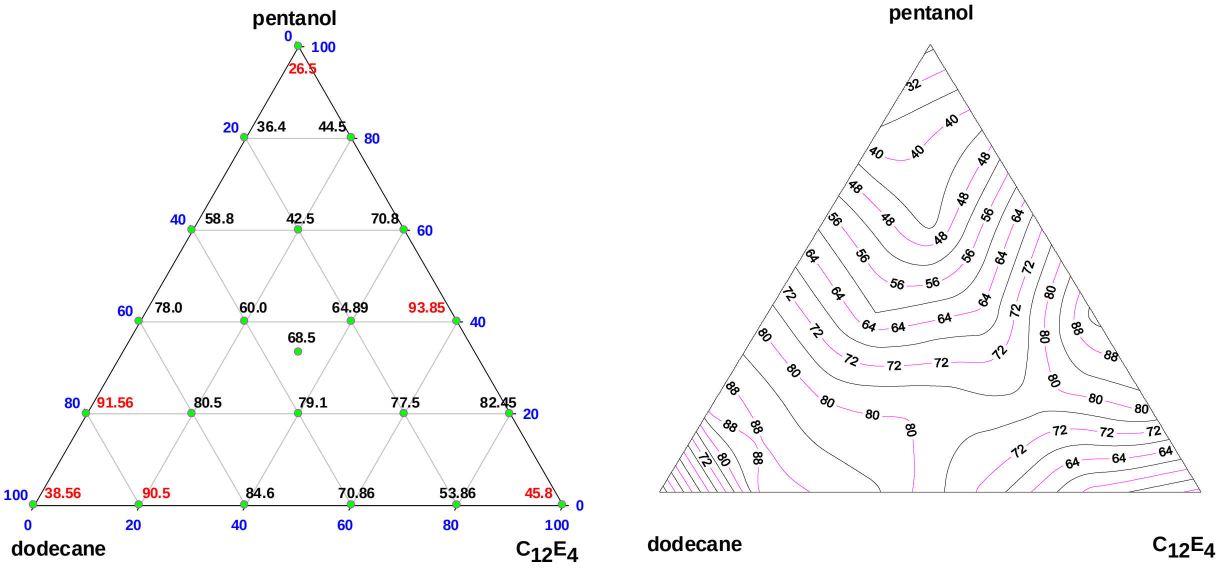
Fig. 72. Effect of dodecane-$C_{12}E_4$-pentanol combinations on clean coal selectivity index B at total dosage of 8 g/kg applying DCF/A procedure. Concentration ratios of the three reagents can be read from the plot. a) response map studied combinations and obtained results. Circles indicate studied points and values represent selectivity index B, b) selectivity index B contour map based on data from Fig. 72a

Figure 72b shows that the selectivity contours assume their lowest values when using pentanol alone. The contours go in an ascending order parallel to each other when pentanol was modified with dodecane or $C_{12}E_4$. They also have a concave shape starting at a low $C_{12}E_4$ level and ending at much higher dodecane levels. It shows that $C_{12}E_4$ is more effective than dodecane. Three main conclusions can be seen from this Figure:

- dodecane levels have the lowest influence on separation efficiency index B

- pentanol levels have positive effect on the separation efficiency up to a certain level after which the effect will be negative
- $C_{12}E_4$ levels have the highest influence on the separation efficiency with a continuous positive effect.

For the higher dosage (16g/kg), Fig. 73a-b shows the clean coal yield and its contour map with the results obtained for one- and two-reagent systems. Figure 73a illustrates that the maximum clean coal yield obtained applying the different combinations of the three reagents at the 16 g/kg level is approximately 80.0 %. It was achieved twice (80.5 and 79.1%) at the dodecane:$C_{12}E_4$:pentanol ratio of 3:1:1 and 2:2:1, that is the same as at the lower level of 8g/kg. At the same time, better clean coal yields were achieved using the two-reagent systems at the same dosage (90.5% for dodecane-$C_{12}E_4$ at the 4:1 ratio), 91.56% for dodecane-pentanol at the 4:1 ratio, and 93.85% $C_{12}E_4$-pentanol at the 3:2 ratio).


a) clean coal yield response map

b) clean coal yield contour map

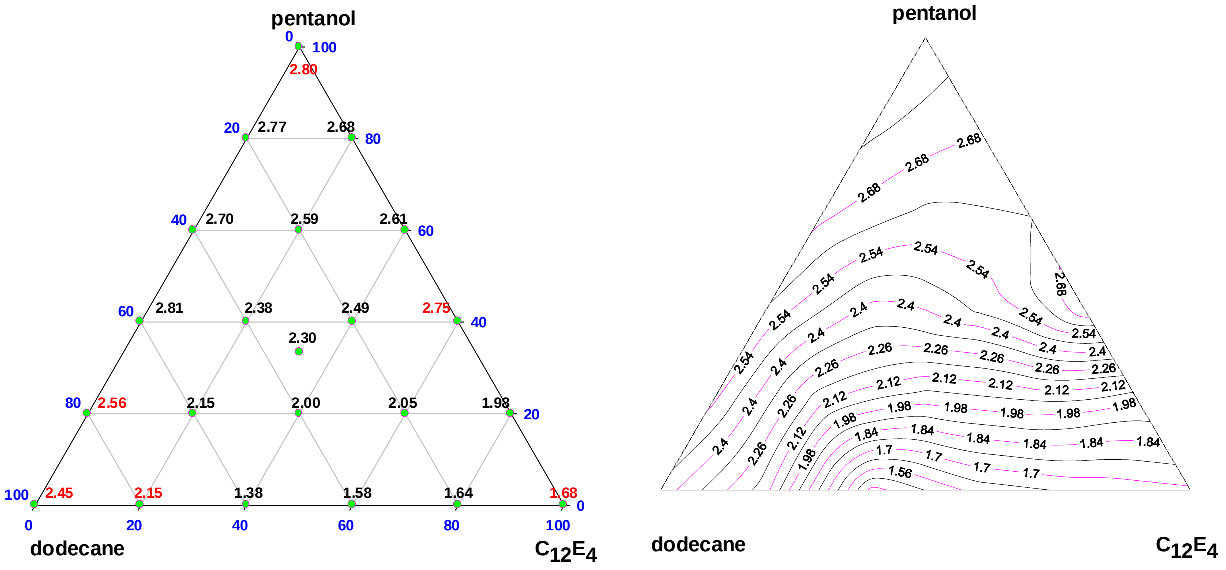
Fig. 73. Effect of dodecane-$C_{12}E_4$-pentanol combinations on clean coal yield at total dosage of 16 g/kg applying DCF/A procedure. Ratios between three reagents can be read from the plot. a) response map for studied combinations and obtained results, circles indicate studied points and values represent clean coal yield in %, b) clean coal yield contour map based on data from Fig. 73a

Figure 73b shows the clean coal yield contour map drawn from Fig. 73a using the Surfer V. 7 software. It shows parallel contours having low values near the plot apexes increasing in the direction of the two- and three-reagent combinations. They are crowded near the apexes that reflect the sensitivity of yield to reagent modification. The contours obtained in this dosage (16 g/kg) of the chemicals have minor differences if compared to those obtained with the lower level (8g/kg). The same conclusion, noticed for the lower dosage, is again being confirmed at a higher level. The three-reagent combinations did not show any improvement over those obtained with the two-reagent systems.

Figure 74a-b depicts the clean coal ash content response and iso-response (contour) maps obtained applying the different combinations of the three reagents together with the necessary results for one- and two-reagent systems at the dosage level of 16 g/kg. It can be seen from Fig. 74a that the cleanest product resulted from applying different three-reagent combinations has an ash content of 2.0% at the dodecane:$C_{12}E_4$:pentanol ratio of 2:2:1. This is not in agreement with the ratios providing the cleanest product at the lower level of the reagents (8g/kg). It also shows that cleaner coal products can be obtained applying two-reagent systems or even one-reagent systems. For example, products having 1.38, 1.58, and 1.64% ash were obtained using different dodecane/$C_{12}E_4$ ratios as a two-reagent system while product having ash content of 1.95% was obtained using the pentanol:$C_{12}E_4$ ratio of 1:4. Meanwhile, the $C_{12}E_4$ one-reagent system provided a product having ash content of 1.68%.

Figure 74b shows clean coal ash contours drawn from Fig. 74a. It reflects parallel convex contours representing clean coal products near the dodecane-$C_{12}E_4$ border with an increase in clean coal ash content when increasing the pentanol level. The worst product was produced with 16g/kg of pentanol alone.

Figure 75a-b shows selectivity or separation resulted from the total dosage of 16 g/kg. Figure 75a indicates that the best three-reagent combination leads to selectivity index B of 0.699 at the dodecane:$C_{12}E_4$:pentanol ratio of 2:2:1 compared to a maximum B of 0.528 at the dodecane:$C_{12}E_4$:pentanol ratio of 1:3:1 obtained with the lower dosage of the three reagents (8 g/kg). It also confirms the preference of two-reagent over three-reagent systems, where a selectivity index of 0.858 was obtained using the dodecane:$C_{12}E_4$ ratio of 4:1 and 0.745 when using the pentanol:$C_{12}E_4$ ratio of 2:3.


a) clean coal ash content response map

b) clean coal ash contour map

Fig. 74. Effect of dodecane-$C_{12}E_4$-pentanol combinations on clean coal ash at total dosage of 16 g/kg applying DCF/A procedure. a) response map with studied combinations and obtained results, circles indicate studied points and values represent clean coal ash %, b) clean coal ash contour map based on data from Fig. 74a

Figure 75b shows that the selectivity contours are of their lowest values when using pentanol alone. The contours go in an ascending order parallel to each other when pentanol was modified with dodecane or $C_{12}E_4$. They also have a concave shape starting at a low $C_{12}E_4$ level and ending at much higher dodecane levels. It shows that $C_{12}E_4$ is more effective than dodecane even at a higher dosage level of the three reagents. The main conclusions from this Figure are:

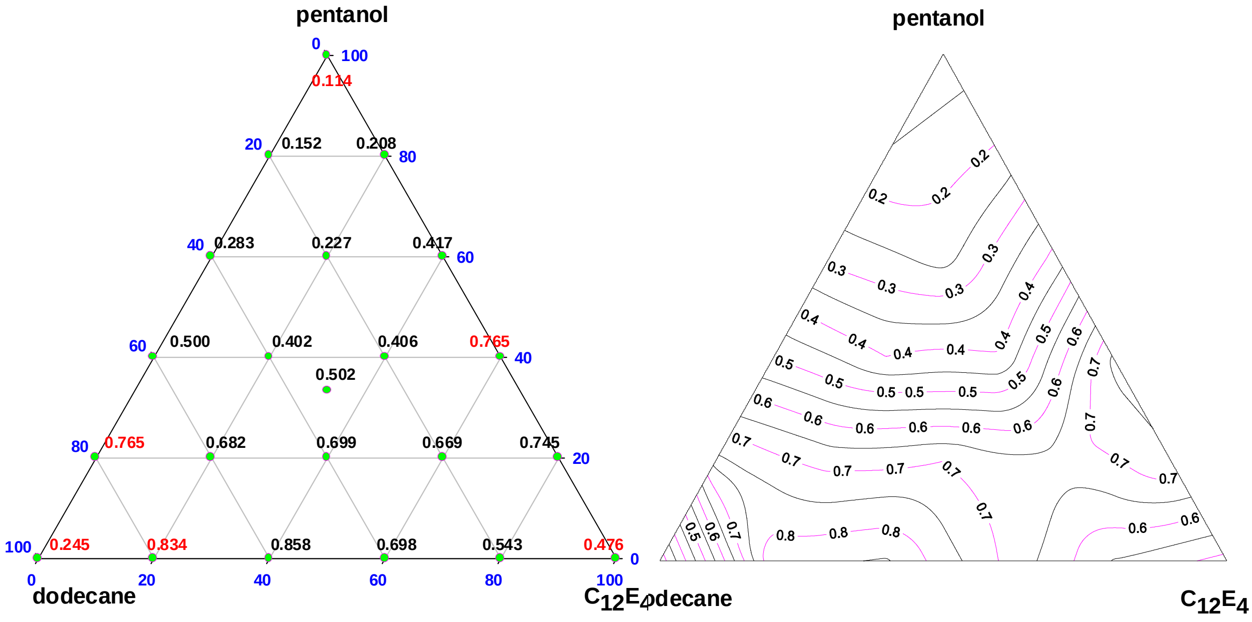
-increasing the pentanol level by 20% leads to a moderate improvement in the separation efficiency

-any further increase of pentanol dosage provides negative effects in the separation efficiency as it is clear for the 40% and 60% pentanol levels

-without dodecane, the separation efficiency is a result of changing the two reagents (pentanol:$C_{12}E_4$) ratio alone. It was found to be of a moderately high value. The separation efficiency might be slightly improved by increasing the dodecane level up to 20 %. Any further increase of the dodecane dosage provides negative effects on the separation efficiency

-dodecane levels have the lowest influence on the separation efficiency

-$C_{12}E_4$ levels have the highest influence on the separation efficiency with a continuous positive effect.


a) selectivity index B response map

b) selectivity index B contour map

Fig. 75. Effect of dodecane-$C_{12}E_4$-pentanol combinations on coal selectivity index B at total dosage of 16 g/kg applying DCF/A procedure, a) response map for studied combinations and obtained results, circles indicate studied points and values represent selectivity index B, b) coal selectivity index B contour map

Results of different combinations of the applied three reagents at both of the considered levels (8 and 16 g/kg) illustrated that the three-reagent combinations did not result in any improvements compared to the two-reagent systems even when they were applied in the direct-contact DCF/A procedure. In this system, for example, the highest yield product, cleanest product, and hence highest selectivity were obtained on the outside borders of the Gibbs plot which represent one- and two-reagent combinations. Therefore, the next section is devoted to investigate the microemulsion structure created from different combinations of the dodecane-$C_{12}E_4$ two-reagent system in water for flotation of the studied difficult-to-float oxidized coal applying the direct-contact flotation DCF/B procedure. For comparison purposes other structures as emulsions, and liquid crystals formed with the same two-reagents in water will be also considered.

6.3.2. Flotation results using direct-contact flotation procedure (DCF) version B

Application of the direct-contact flotation (DCF/A) procedure in comparison to the NCF method provided better flotation responses for clean coal yield, ash content, and selectivity index B. However, the high reagent consumption associated with the DCF/A technique can be attributed to coal surface nanoscale roughness (Drefahl et al., 1998; Brown and Moudgil, 2004) and reagent adsorption into surface pores (Laskowski, 2001). In the next section, different water-surfactant/s mixtures providing various structures, including microemulsions, will be investigated applying the direct-contact flotation procedure. It is called DCF version B or DCF/B procedure. In this procedure, the chemicals are not added one-by-one anhydrous form as in DCF/A but as a mixture of reagents in water, and are added before water is introduced to the flotation system.

6.3.2.1. DCF/B of coal in the presence of different forms or species created by a single reagent in water

Dodecane-$C_{12}E_4$-water phase diagram (Fig. 33) showed that different concentrations of either dodecane or $C_{12}E_4$ in water lead to the formation of different structures. The structures were different emulsion of dodecane, while for $C_{12}E_4$ they were normal micelles at low concentrations of $C_{12}E_4$ in water, liquid crystal structure for intermediate concentrations, and inverted micelles at the $C_{12}E_4$ concentrations in water greater than 80%. Different concentrations of either dodecane in water or $C_{12}E_4$ in water were selected as reagent stocks for flotation of the investigated difficult-to-float oxidized coal at a constant dosage level of 10 g/kg. Details are shown in Table 22.

Table 22. Reagent-water concentrations and their corresponding forms (structures) according to phase diagram shown in Fig. 33. They were used for flotation of coal applying DCF/B procedure

Series #	Experiment # and details			
1 (dodecane in water)	exp. #	1	2	-
	wt. %	20	80	-
	structure	O/W emulsion	W/O emulsion	-
2 ($C_{12}E_4$ in water)	exp. #	1	2	3
	wt. %	10	50	90
	structure	normal micelles	liquid crystals	inverted micelles

Figure 76 shows the clean coal yield obtained in this series and for comparison, selected results obtained with the DCF/A procedure. It shows that there is some improvement in the flotation yield when either normal or inverted micelles of $C_{12}E_4$ were used in the adsorption stage. Normal and inverted micelles of $C_{12}E_4$ lead to approximately the same clean coal yield.

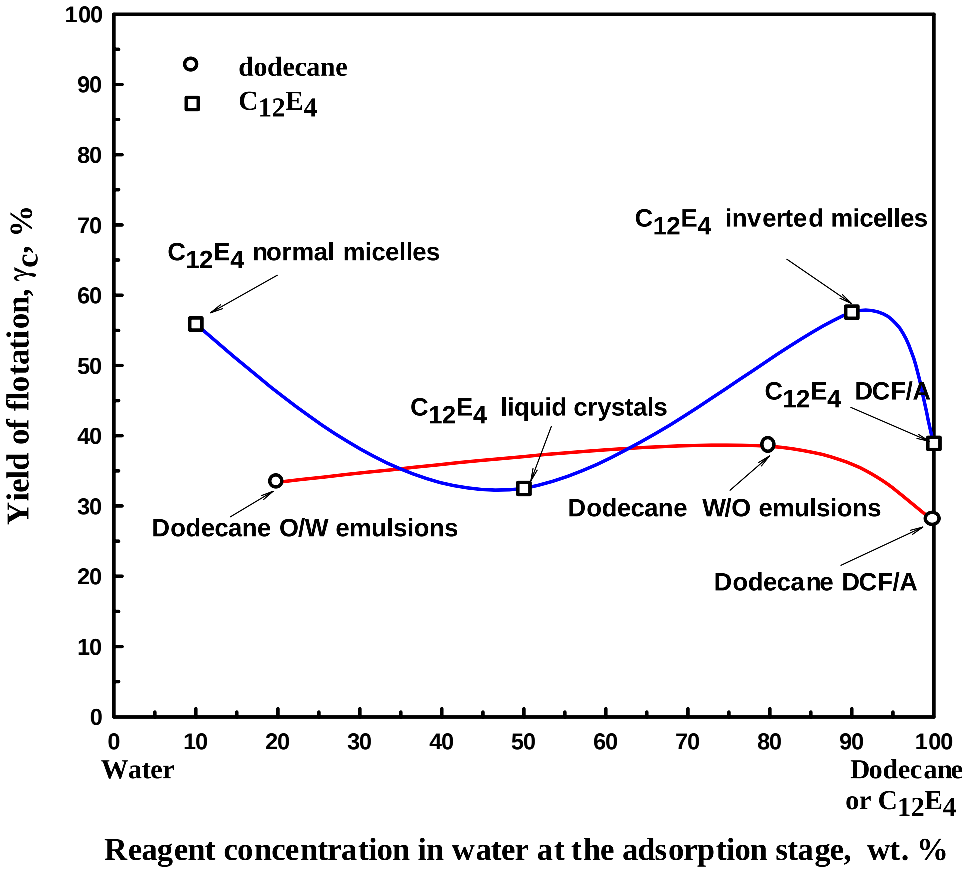


Fig. 76. Effect of 10g/kg of single reagent (dodecane or $C_{12}E_4$)-water structures at adsorption stage on clean coal yield applying DCF/B procedure

Figure 77 shows Fuerstenau’s plot illustrating selectivity index B for the different studied structures considered in both dodecane and $C_{12}E_4$ series. The values of the selectivity indices are shown in Table 23.

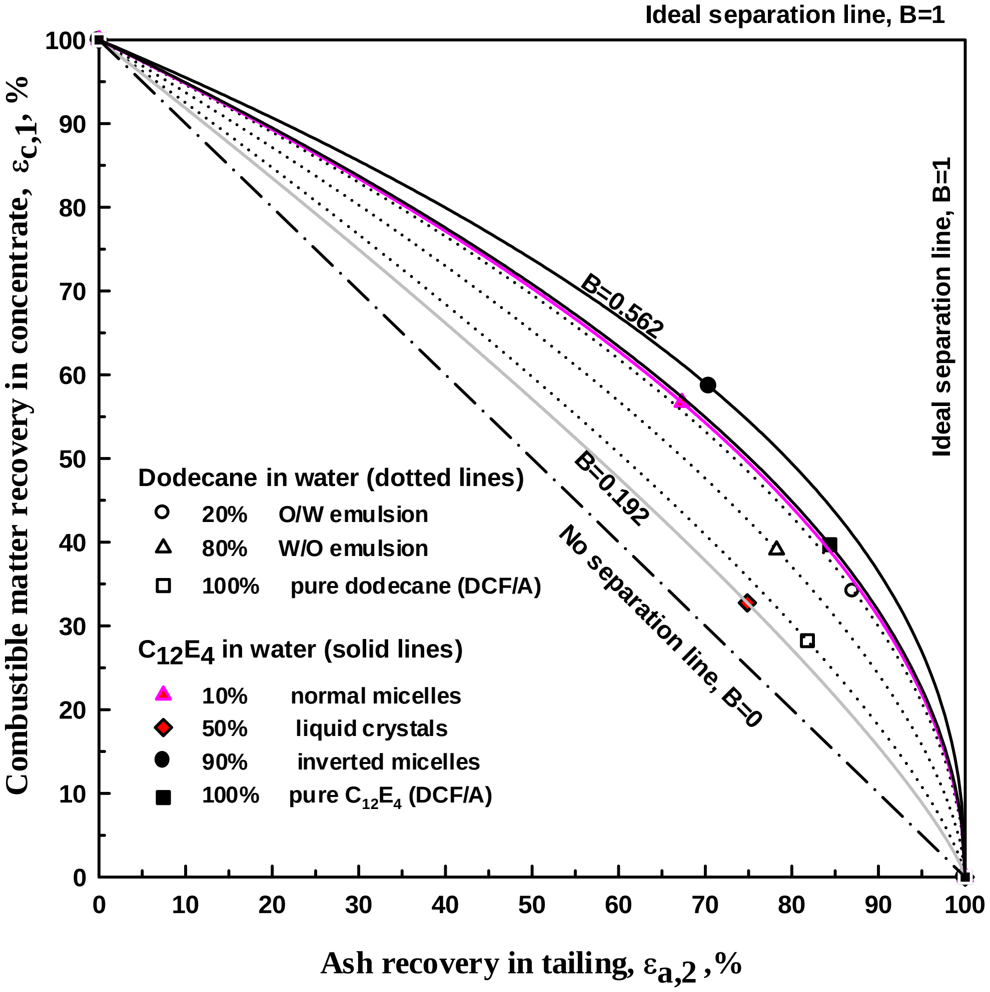


Fig. 77. Fuerstenau's plot showing effect of single reagent-water structure on the separation of coal at a dosage of 10 g/kg applying the DCF/B procedure

Table 23 Selectivity index B using different structures of either dodecane in water or $C_{12}E_4$ in water at dodecane or $C_{12}E_4$ dosage of 10 g/kg applying DCF/B procedure

Series #	Experimental details and results				
1 (Dodecane in water)	wt. %	20	80	100*	
	structure	O/W emulsion	W/O emulsion	-	
	selectivity B	0.476	0.384	0.257	
2 ($C_{12}E_4$ in water)	wt. %	10	50	90	100*
	structure	normal micelles	liquid crystals	inverted micelles	-
	selectivity B	0.492	0.192	0.562	0.502

*DCF/A procedure

Figure 77, together with Table 23, show that selectivity index B, when using 10 g/kg of dodecane (prepared as different forms in water), ranges from 0.257 to 0.476. The worst separation, when using dodecane, was encountered using pure dodecane without previous emulsification of the stock i.e. with the DCF/A technique providing selectivity index B equal to 0.257. In the case of using 10 g/kg of $C_{12}E_4$ different structures in water, the lowest selectivity was 0.192. It was obtained using the liquid crystal form. The low clean coal yield together with the low separation selectivity related with this structure show its disability to adsorb on the coal surface. On the other hand, $C_{12}E_4$ concentrations in water corresponding to either normal or inverted micelles lead to higher selectivity compared to that of liquid crystal that is 0.492 and 0.562 respectively.

Comparison of the selectivity indices for both of the two considered reagents (dodecane and $C_{12}E_4$) showed a partial conflict with the Jia et al., (2000) recommendations of preference for ethoxy compounds in oxidized coal flotation over hydrocarbons. As it is clear in our case, the 20% O/W emulsion of dodecane with selectivity index of 0.476 resulted in better separation in comparison to ethoxy compound with the liquid crystal structure for which the selectivity index B was equal to 0.192. Yet, there exist an agreement with Jia et al., (2000) that the right structure of C_xE_y compound (normal micelles, inverted micelles) provide a better separation than the best dodecane structure.

Generally, this series showed that a single reagent-water structure has a great effect on the flotation response when applying the direct-contact flotation (DCF/B) procedure.

6.3.2.2. DCF/B of coal in the presence of different forms or species created by two reagents in water (emulsions, microemulsions, etc.)

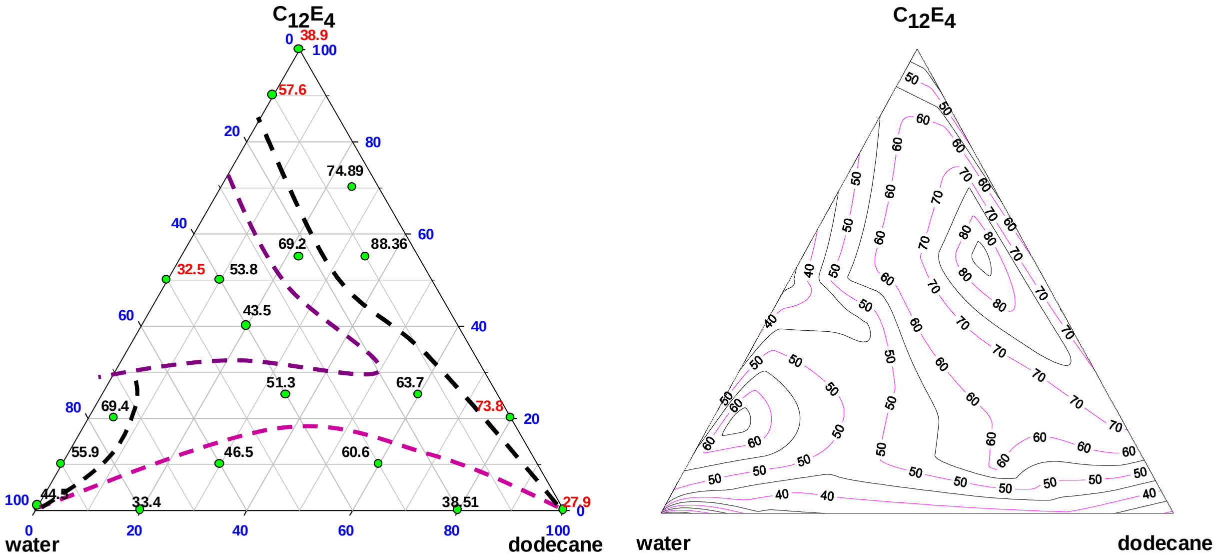
Previous results showed that the flotation of oxidized coal depends on the reagent structure in water. Therefore, microemulsions formed from different combinations of dodecane and $C_{12}E_4$ in water were used for coal flotation applying the DCF/B procedure at the dodecane+$C_{12}E_4$ dosage of 10 g/kg. For comparison purposes, other structures were tested at the same 10 g/kg of dodecane+$C_{12}E_4$. The different dodecane-$C_{12}E_4$-water combinations considered in this series and their corresponding structures are shown in Table 24.

Table 24. Different combinations of dodecane-$C_{12}E_4$-water system and their corresponding structures used for flotation of oxidized coal at dodecane+$C_{12}E_4$ dosage of 10 g/kg applying DCF/B procedure

Exp. #	Dodecane, %	Water, %	$C_{12}E_4$, %	Structure
1	30	60	10	O/W emulsion
2	60	30	10	W/O emulsion
3	5	75	20	O/W microemulsion
4	35	40	25	Bicontinuous
5	60	15	25	Bicontinuous
6	20	40	40	Liquid crystal
7	10	40	50	Liquid crystal
8	22	23	55	Bicontinuous
9	35	10	55	W/O microemulsion
10	25	5	70	W/O microemulsion

Figure 78a-b shows the clean coal yield and its contour map, obtained with the different studied combinations shown in Table 24, applying the DCF/B procedure at 10 g/kg dosage of $C_{12}E_4$+dodecane, together with the necessary results of previous tests.

Figure 78a shows that the highest clean coal yield in this series was obtained using the W/O microemulsions. A maximum clean coal yield of 88.4% containing 2.48% ash was obtained, compared with 73.8% yield and 1.98% ash when using the same dosage of the same system but applying the DCF/A procedure. This maximum clean coal yield is corresponding to weight percentage of dodecane, water, and $C_{12}E_4$ of 35.0, 10.0 and 55.0 %, i.e. at 3.9 and 6.1 g/kg of dodecane and $C_{12}E_4$, respectively. It is clear that the dodecane:$C_{12}E_4$ ratio corresponding to the maximum clean coal yield in that case is ~ 1:1.6, compared to 4:1 in the case of the DCF/A procedure. It indicates that the adsorption mechanism in the case of water-reagent structures is completely different from that taking place when applying pure reagents even using the same flotation procedure.



a) clean coal yield response map

b) clean coal yield contour map

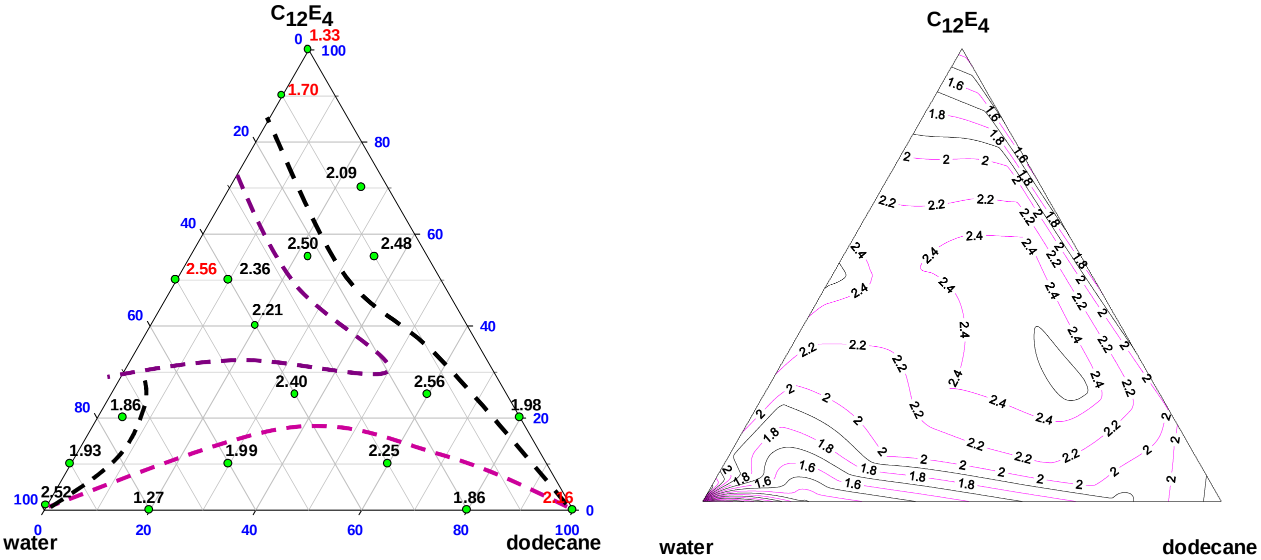
Fig. 78. Clean coal yield response (a) and contour (b) maps for flotation results obtained for different structures of water-dodecane-$C_{12}E_4$ system at dodecane+$C_{12}E_4$ dosage of 10 g/kg using DCF/B procedure

Figure 78b illustrates the yield contours based on the results shown in Fig. 78a. It shows that the yield contours characterize different regions of change. The contours shape is usually dependent on each area shown on the dodecane-$C_{12}E_4$-water phase diagram (Fig. 33). The clean coal yield obtained using different water-reagents structures together with the contour lines change corresponding to the different phase diagram regions indicate the following:

- clean coal yield obtained using the W/O emulsion structure is usually higher than that obtained using the O/W one. This maybe attributed to the fact that the core of the W/O droplet is filled with water apparently providing greater dosage than the actual considered dosage of reagents
- flotation using O/W microemulsion structure in the adsorption stage resulted in a higher clean coal yield than that obtained with any of the emulsion structures. This maybe attributed to the smaller droplets diameter in the case of microemulsion structure leading to a coverage of a higher surface area at the same dosage of the considered reagents. The expected higher surface area coverage provides a higher probability of coal surface hydrophobization, and hence higher yields of flotation

- poor yields encountered using the hexagonal liquid crystal structures maybe attributed to the complexity of the structure together with its high packing factor leading to multilayer adsorption on the coal surface.

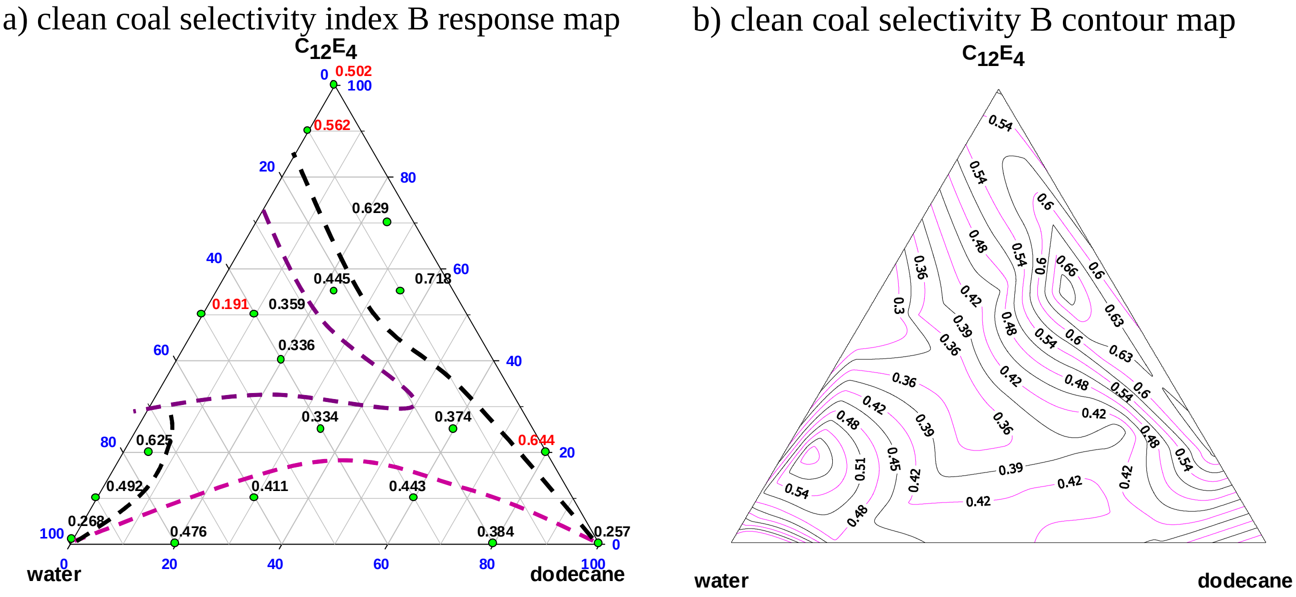
As to the clean coal ash, its response and contour maps are shown in Fig. 79a-b. The contours obtained for the ash content are completely different from those encountered for the yield. This shows that the different structures present in the phase diagram (Fig. 33) have different adsorption mechanisms reflecting various yields and associated ash contents responses. In general, one can conclude from this series of experiments that applying either one- or two-reagent structures for flotation of oxidized coal leads to an improvement not only of the clean coal yield but also the selectivity. Figure 80 shows a superior selectivity can be achieved in a narrow region of the dodecane-$C_{12}E_4$-water structures applied during the adsorption stage. This region occurs in the microemulsion area.



a) clean coal ash content response map

b) clean coal ash contour map

Fig. 79. Clean coal ash content response (a) and contour (b) maps for coal flotation with different structures of water-dodecane-$C_{12}E_4$ system at dodecane+$C_{12}E_4$ dosage of 10 g/kg using DCF/B procedure



a) clean coal selectivity index B response map

b) clean coal selectivity B contour map

Fig. 80. Clean coal selectivity index B response (a) and contour (b) maps resulted from flotation with different structures of water-dodecane-$C_{12}E_4$ system at dodecane+$C_{12}E_4$ dosage of 10 g/kg using DCF/B procedure

6.3.3. Evaluation of coal flotation results applying both direct-contact flotation procedures (DCF/A, DCF/B)

The reagent combinations studied applying the direct-contact flotation DCF/A procedure for flotation of oxidized coal revealed the following conclusions:

-although one-reagent direct-contact flotation resulted in the worst yield compared to two-, and three-reagents for DCF, yet results was of better in comparison with those obtained in case of normal-contact flotation procedure

-using two reagents under constant dosage of 8 g/kg with different reagent ratios revealed a co-existence of positive synergetic effects at a ratio depending on the type of the two reagents under investigation. The product obtained from such a series is better than that obtained from the same series using normal flotation procedure, as for as the separation efficiency is concerned

-changing the total dosage of the two reagents at their optimum ratio leads to a change in the results of separation. It tells that the separation efficiency depends not only on the two reagents ratio but also on their total dosage as well

-comparing the results for three reagents under different combinations at tow total dosage levels (8 and 16 g/kg) and that of two-reagent at the same dosage levels indicates that two-reagent systems are preferable from both the quantity and the quality point of view

-the DCF/B version showed that the reagent-water structures have a great effect on the flotation response

6.4. Flotation in the $C_{12}E_4$-dodecane-water microemulsion region with water from the coal moisture

It is clear from the conducted studies that flotation of oxidized coal depends on the flotation procedure and reagents structure during the adsorption stage. The best results were obtained at certain water content (~10%) in the dodecane-$C_{12}E_4$ mixture forming microemulsion. This is a good factor because it is convenient to prepare reagent containing some water. Also, the run-of-mine coals contain always some moisture. In addition to that, stored oxidized coals have a tendency to adsorb water from the atmosphere. Therefore, a new series of experiments was designed to determine the interactions that may take place between pure reagents and coal moisture when applying the direct-contact flotation procedure. For this reason, an artificial moisture was admitted to the oxidized coal sample by direct expose of its surface to the water vapors.

The two-reagent dodecane+$C_{12}E_4$ system was used in this investigation. The total dosage of the two reagents was 10 g/kg and was calculated on the basis of grams of reagents per kg of dry (moisture free) coal. At the same time, the $C_{12}E_4$:dodecane ratio was varied from 1:9, 1:4, 1:1 to 4:1, that is from 10, 20, 50, to 80%, respectively. Figure 81 shows the effect of coal moisture content on the clean coal yield obtained at different ratios of the two reagents. It illustrates that at a high $C_{12}E_4$ content some moisture is beneficial for the studied coal flotation.

The results are consistent with experiments run in the presence of the microemulsions which showed that there is a small microemulsion (not anhydrous reagents) region providing superior results. This is presented in Fig. 82 which shows the water dilution lines associated with the studied dodecane-$C_{12}E_4$ ratios together with the dodecane-$C_{12}E_4$-water phase diagram, and the microemulsion region providing the best flotation results.

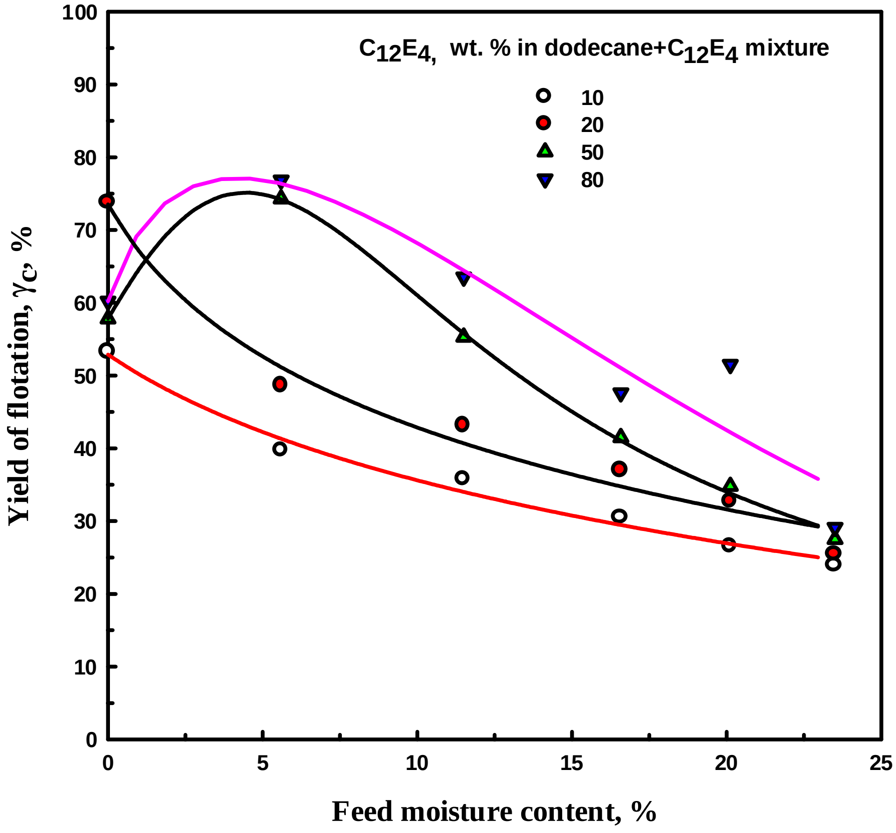


Fig. 81. Effect of moisture content on clean coal yield using 10 g/kg dodecane+$C_{12}E_4$ as pure reagents at different ratios applying DCF/A procedure

For the $C_{12}E_4$:dodecane ratio of 1:9 (10% $C_{12}E_4$), and 1:4 (20% $C_{12}E_4$), Fig. 81 shows a continuous decrease in the clean coal yields. The water dilution lines of such $C_{12}E_4$:dodecane ratios (Fig. 82) reflect the existence of different forms of emulsion structures. The decrease in the clean coal yield maybe attributed to the fact that at the zero moisture content, the flotation process is similar to that of the pure-reagent direct-contact process providing a high clean coal yield. At the same time, increasing the coal moisture content did not provide the theoretically expected emulsions of flotation reagents with water coming from the coal moisture. This maybe attributed to the fact that emulsions cannot be formed spontaneously but they need external work to lower the reagents-aqueous interfacial tension. At the same $C_{12}E_4$/dodecane mentioned ratios (1:9 and 1:4) and with further increase in the coal moisture content, the clean coal yields decrease drastically. The obtained clean coal yield at ~25% coal moisture tend to be very close to the results obtained applying the normal-contact flotation procedure. This can lead to the idea that the normal-contact flotation is a direct-contact flotation in which the used coal can be considered as having high moisture contents (>25%).

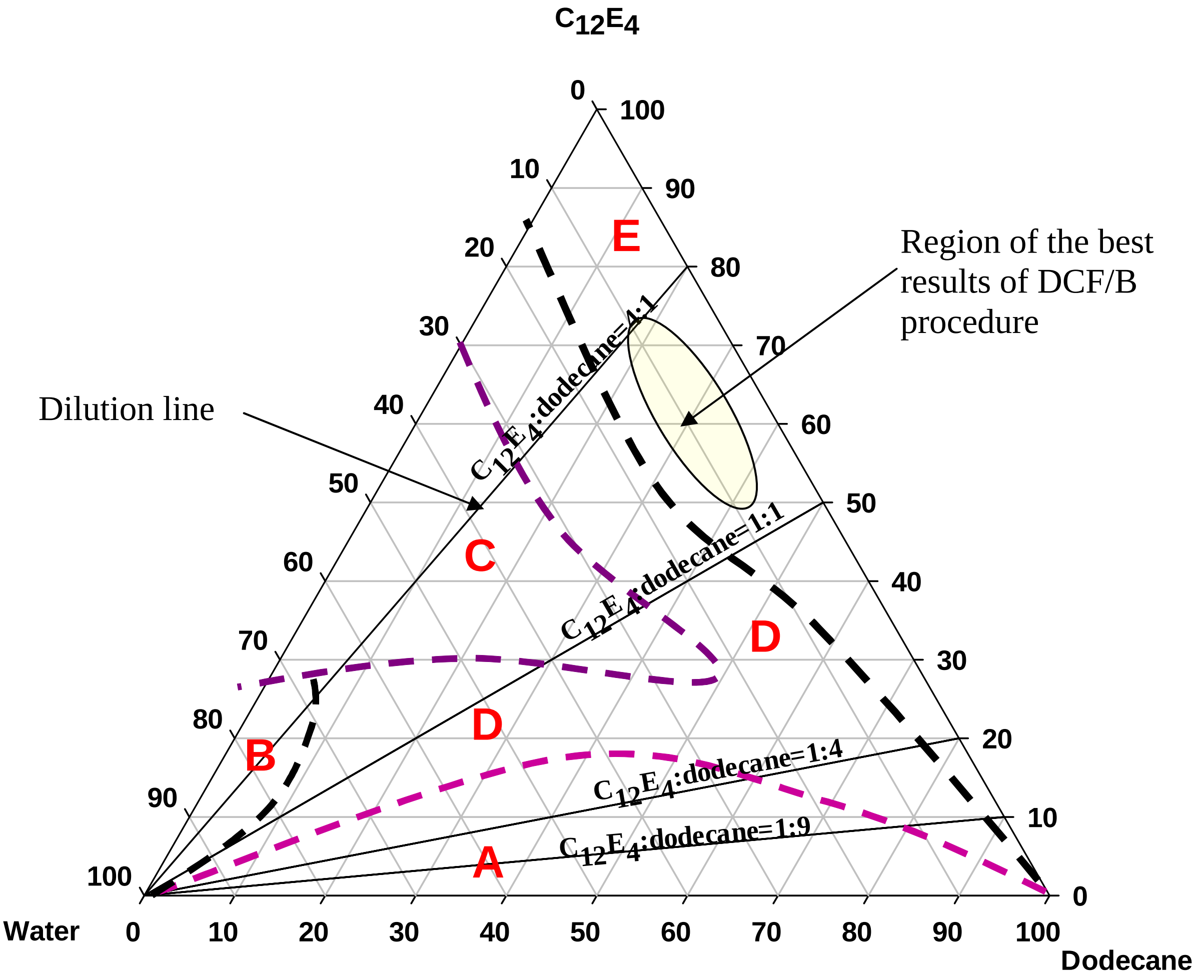


Fig. 82. Phase diagram of water-dodecane-$C_{12}E_4$ system at 25°C showing dilution lines when changing coal moisture at different dodecane/$C_{12}E_4$ ratios. A- different forms of emulsions, B- normal micelles and O/W microemulsions (the border between the sub-areas is not shown) C- hexagonal liquid crystals, D- bicontinuous liquid crystals, and E-inverted micelles and W/O microemulsions (the border between the sub-areas is also not shown)

The investigation with the 1:1 $C_{12}E_4$/dodecane ratio (i.e. 50% $C_{12}E_4$) (Fig. 81) revealed moderate improvement of the flotation results at a low moisture content followed by a continuous decrease in the clean coal yields with the moisture content incraese. Comparing the obtained results with the possible structures that can be formed along the water dilution line corresponding to this ratio (Fig. 82) explains the obtained results. The slightly lower clean coal yield obtained at a zero moisture content can be attributed to the consumption of reagents by pores and nanoscale surface roughness of coal as it was discussed previously. On the other hand, the moisture of coal participates in a spontaneous formation of O/W microemulsions. The spontaneously formed microemulsions improves the clean coal yield by reducing reagents adsorption in coal pores leading to apparent increase in reagents dosage. The theoretically expected liquid crystals, due to any increase in the coal moisture content, as shown by the water dilution line, were not created. This is maybe the main reason for why the flotation results, at higher moisture contents, were not in agreement with that obtained using the reagents structures applying direct-contact procedure. The same explanation is also valid for the clean coal yields obtained when investigating the $C_{12}E_4$/dodecane ratio of 4:1 or 80% $C_{12}E_4$, (Figs. 81-82). The clean coal yield plateau formed at high moisture content in coal (Fig. 81) maybe attributed to the spontaneous formation of the O/W microemulsions (Fig. 82).

The results obtained in this series cannot be easily compared with the results obtained from coals containing the same natural moisture contents. This is so because the artificially moist coal has about 90% of its moisture presents at the surface, while in case of coal with natural moisture the majority of its moisture presents in pores and so the chance of its attachment to reagent is fairly low.

CONCLUDING PART

7. General discussion

Difficult-to-process materials require special approaches for their upgrading. One of these approaches, the use of concentrated reagents in a form of either anhydrous reagents or aqueous microemulsion, is presented in this thesis. It is designed for materials which are processed by flotation, such as oxidized coals. The oxidized coals have high surface oxidation, and hence high hydrophilicity, that opposes rendering them into hydrophobic and floatable materials using typical flotation reagents. The proposed approach relies on the application of a mixture of reagents consisting of oily collector, frother, and promoter in anhydrous or concentrated forms as microemulsions. This is in contrast with typical flotation procedures in which diluted aqueous solutions of flotation reagent are applied. In the case of microemulsions, they can be formed either from the flotation reagents and water or with water coming from the coal moisture. This approach allows the surface to become hydrophobic. Once the surface is rendered hydrophobic, its further contact with water does not change much the created hydrophobicity leading to better results of flotation. This approach was successfully tested on a Polish difficult-to-float oxidized coal.

For a comparison purpose, the upgrading of coal was tested applying the traditional flotation procedure first. In this approach, coal was suspended in water and contacted with flotation reagents in diluted aqueous solutions. This traditional flotation procedure was in this thesis referred to as the normal-contact flotation or shortly NCF. It was investigated using different reagents in various combinations and concentrations. There were two-modifications of the NCF procedure. The first version of NCF relied on the addition of flotation reagents to coal aqueous suspension one-by-one, while the second version, NCF/B, was based on the addition of flotation reagents not one-by-one but as their mixtures. Figure 83 presents the best yields of flotation obtained using either one, two, or three flotation reagents applying the NCF procedure. It shows that the NCF/A procedure provided maximum clean coal yields of ~37% with dodecyl tetra(ethylene glycol) ether ($C_{12}E_4$) at 10g/kg, ~61% using $C_{12}E_4$+pentanol (at the 3:2 ratio and dosage of 10 g/kg), and ~52% with the dodecane-$C_{12}E_4$-pentanol three-reagent system (8 g/kg, dodecane:$C_{12}E_4$:pentanol ratios of 1:2:2 or 1:1:3). The dodecane-$C_{12}E_4$ mixture, investigated by applying the NCF/B procedure, resulted in a similarly poor flotation yield of ~59.5% at 10 g/kg using a mixture of dodecane+$C_{12}E_4$+water at the ratio of 5:14:1. This indicates that the maximum flotation yield for the investigated coal, using the NCF procedure and different reagents, is less than ~60%, which is a poor response taking into account the fact that coal contain only 3.8% of ash.

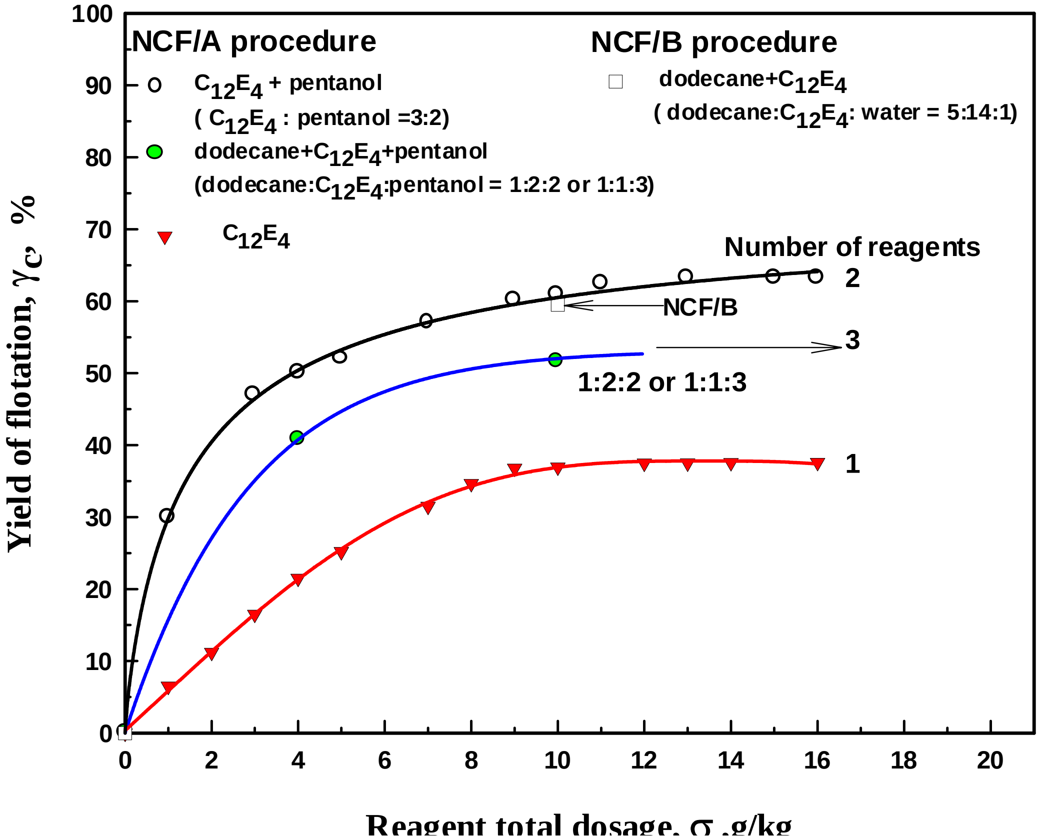


Fig. 83. Flotation results for either one-, two-, or three-reagent systems providing the greatest clean coal yields applying NCF/A procedure. One best result (□) for NCF/B procedure using dodecane+$C_{12}E_4$+water is given for comparison

Selectivity index B, a measure of the curvature of the separation lines, based on equation 2B and calculated from the formula $\mathbf{B} = \dfrac{\ln(100) - \ln(100 - \varepsilon_{a,2})}{\ln(\varepsilon_{c,1}) - \ln(100 - \varepsilon_{a,2})}$, can be seen in Fig. 84 for the best flotation results. It also confirms poor upgrading results for the investigated coal applying the NCF procedure. The systems leading to the best results applying the NCF procedure can be arranged according to selectivity parameter B (given in parenthesis) as follows:

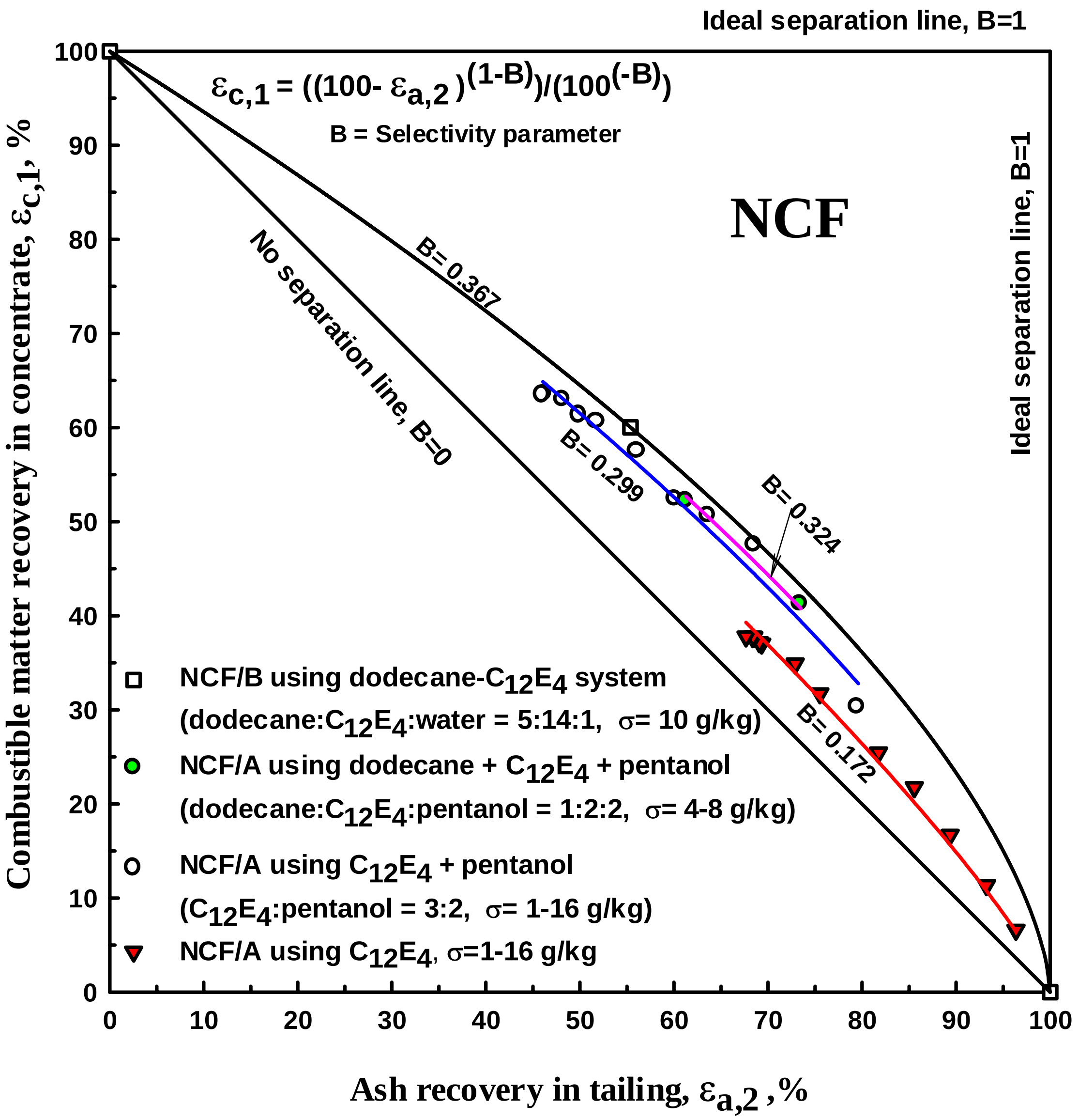


Fig. 84. Ferestenau plot showing separation encountered with the best one-, two-, and three-reagent flotation systems applying normal flotation procedure (NCF/A). Best result of NCF/B procedure is also included (□).

one-reagent(0.17)<two-reagent(0.3)<three-reagent(0.32)<two-reagent (NCF/B)(0.37)
(Selected selectivities for NCF procedure given in Fig. 84) (27)

The poor results obtained using the NCF procedure maybe attributed to the oxidation of the coal surface, while different results are due to the various micelles, and emulsions present in the system during the adsorption stage of the reagents on the surface.

Much better results were obtained applying the direct-contact flotation (DCF) procedure in which concentrated flotation-reagents, having no (version A) or little amount (version B) of water, were mixed with dry coal. The flotation reagents, having little water, formed according to the phase diagram microemulsions which provided effective hydrophobization and cleaning of oxidized coal by flotation. The clean coal yields, obtained for the best flotation results, using either one, two, or three mixed reagents, applying both versions of the DCF procedure, are summarized in Fig. 85.

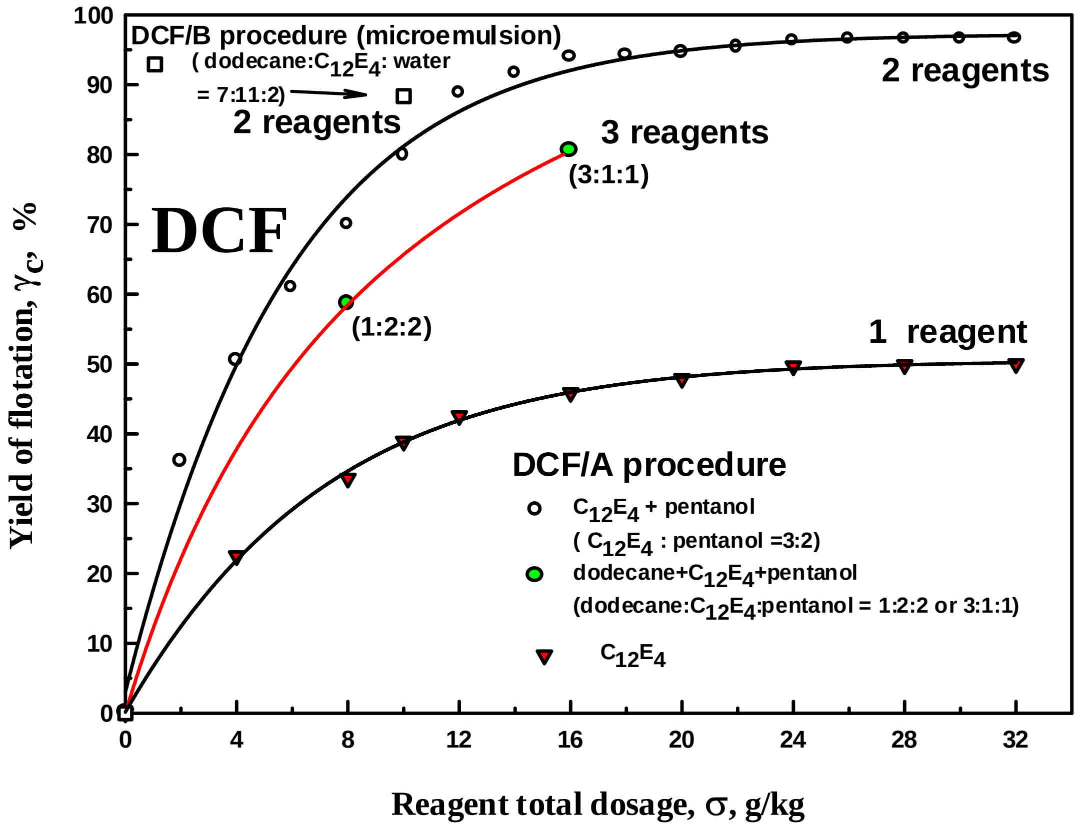


Fig. 85. One-, two-, and three-reagent coal flotation systems providing best clean coal yields applying both versions of direct-contact flotation procedure

The DCF/A procedure provided a clean coal yield of ~50% for $C_{12}E_4$ at 32 g/kg, ~96% using $C_{12}E_4$-pentanol (at the total dosage of 32 g/kg and the $C_{12}E_4$:pentanol ratio of 3:2), and ~81% applying the dodecane-$C_{12}E_4$-pentanol three-reagent system (at 16 g/kg, and the dodecane:$C_{12}E_4$:pentanol ratio of 3:1:1) (Fig. 85).

The application of the DCF/B procedure, using different structures of chemical reagents present in the dodecane-$C_{12}E_4$-water system, provides a high clean coal yield resulting from the use of W/O microemulsion. Using a dosage of 10 g/kg of dodecane+$C_{12}E_4$ in the form of microemulsion (dodecane:$C_{12}E_4$:water = 7:11:2) provided clean coal with the yield of 88.4%.

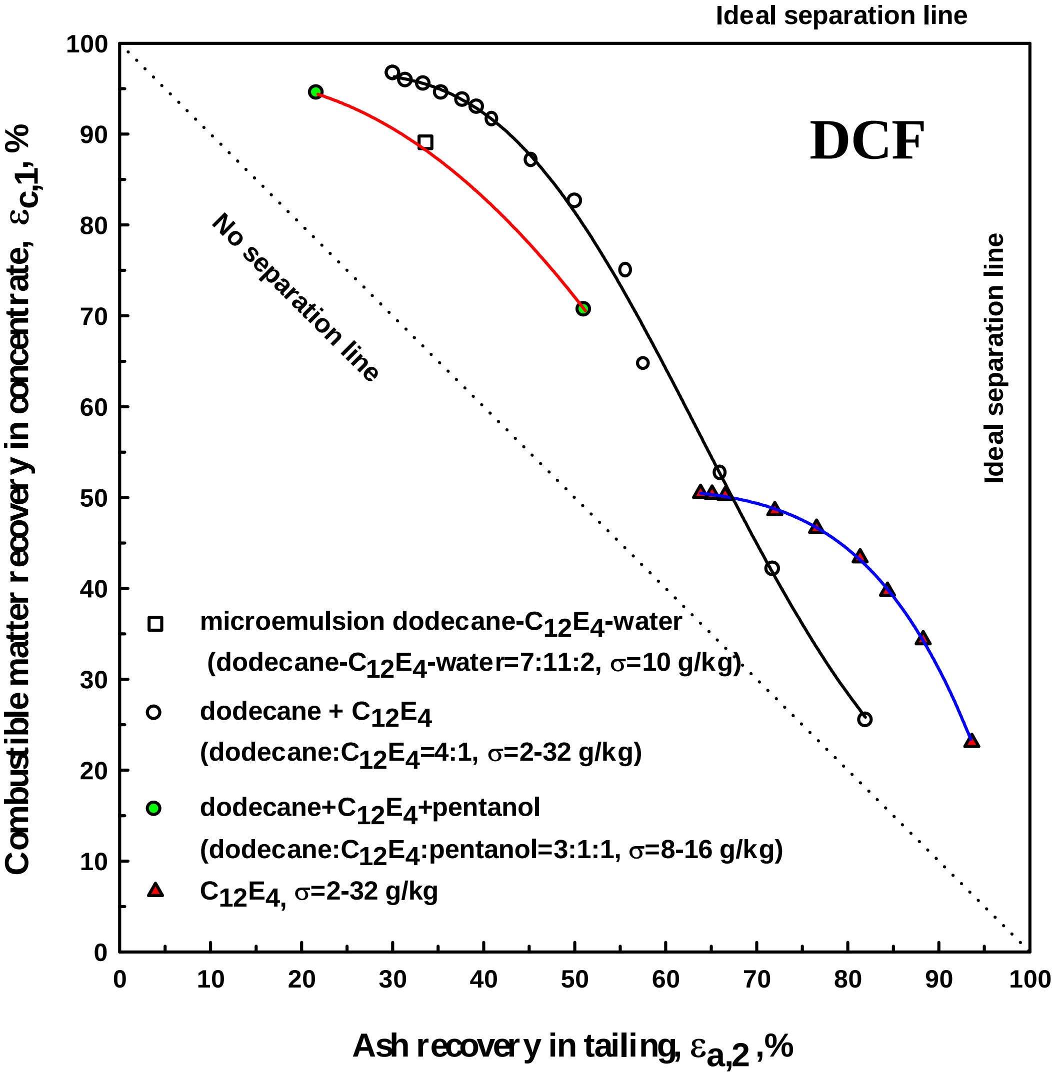


Fig. 86. Ferestenau's plot showing the best separation with one-, two-, and three-reagent systems applying both versions of direct-contact flotation procedure (DCF). The shapes of curves exclude approximation using one-parameter equations given in Table 8.

The selectivity of coal cleaning using the DCF procedure are also very high. However, the shape of the results curve (Fig. 86) is complex and difficult to approximate with the hitherto utilized one-parameter equations providing selectivity index B (or A). Without paying attention to the selectivity index but comparing the location of the real separation line with the location of both no and ideal separation lines, it is obvious that the best selectivity was achieved for the dodecane-$C_{12}E_4$

mixture (24 g/kg). This is so because the recovery of the carbonaceous matter in the concentrate was ~98% and the ash recovery in the tailings was ~34%. Lower selectivity was obtained for the same system when the reagents were introduced as a microemulsion at the dodecane+$C_{12}E_4$ dosage of 10 g/kg and the dodecane:$C_{12}E_4$:water ratio of 7:11:2. Unfortunately, no systematic study was carried out with microemulsion above 10 g/kg. It is expected that applying more than 10 g/kg of dodecane+$C_{12}E_4$ would result in greater yields and selectivity than with an anhydrous reagents. This is because at 10 g/kg dosage of dodecane+$C_{12}E_4$, the microemulsion form provided a higher clean coal yield and deashing selectivity compared to using the same dosage as anhydrous dodecane+$C_{12}E_4$ reagents. Lower selectivity was achieved applying either one- or three-reagent flotation systems.

A comparison of selected selectivity results for the different applied flotation procedures and considered reagents are given in Fig. 87. The results were approximated with selectivity index A (Eq. 1B) using the explicit formula $A = \frac{(\varepsilon_{c,1} + \varepsilon_{a,2} - 100)}{\varepsilon_{c,1} \cdot \varepsilon_{a,2}} \bullet 100$. It shows that for all flotation procedures and reagent systems, the maximum selectivity can be achieved using the dodecane-$C_{12}E_4$ two-reagent system. For instance, at the dodecane:$C_{12}E_4$ ratio of 4:1 and σ= 24g/kg, applying the DCF/A procedure, selectivity index A was found to be 0.917. Other flotation procedures resulted in lower selectivities. However, they can be arranged as follows (selectivity index A, and the dodecane+$C_{12}E_4$ dosage, σ, in g/kg are given in the parenthesis):

NCF/A(0.42,10g/kg)<NCF/B(0.46,10g/kg)<DCF/B(0.76,10g/kg)<DCF/A(0.92,24g/kg)

(Comparison of selected best NCF and DCF selectivities) (28)

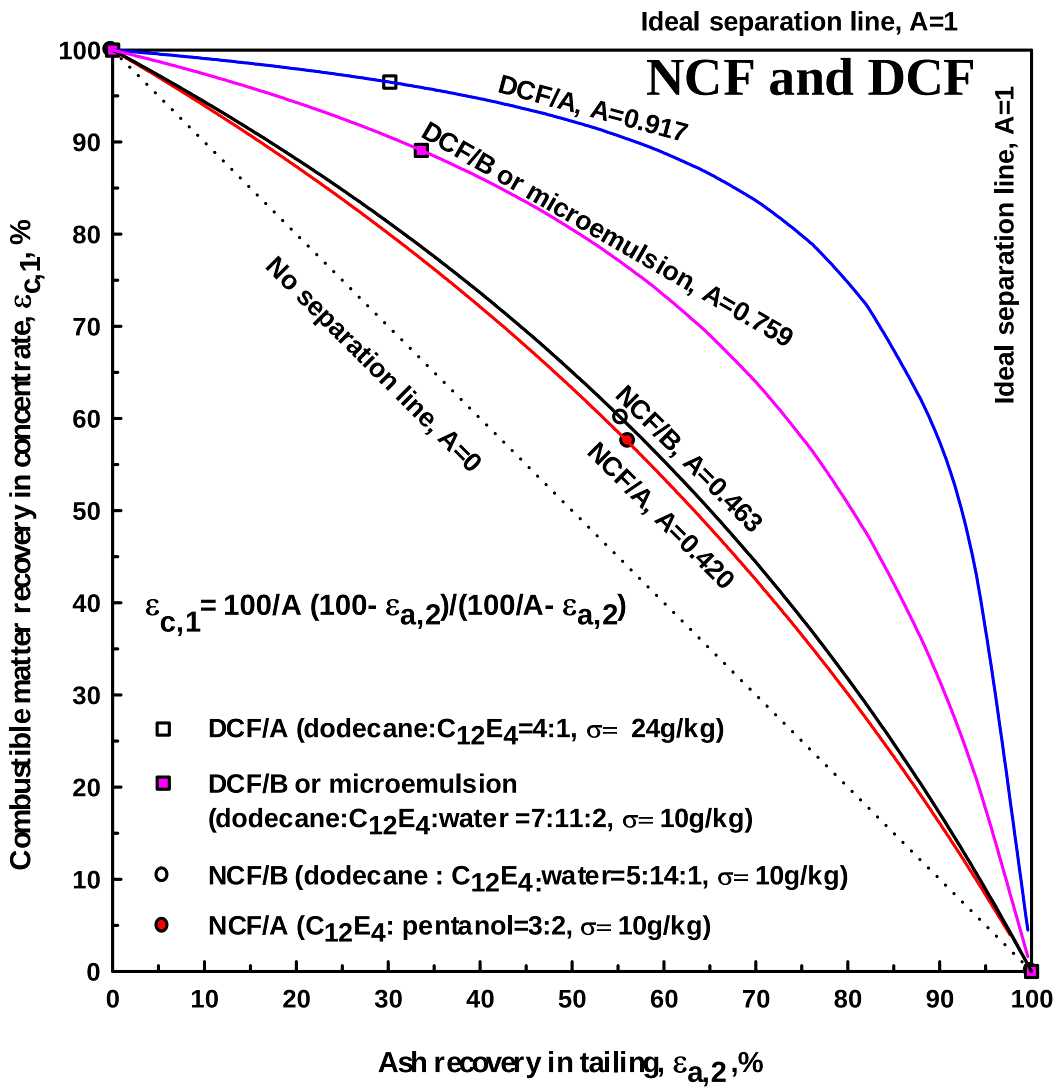


Fig. 87. Ferestenau plot showing comparison of predicted separation results for two-reagent systems assuming symmetrical shape of the separation curves. σ stands for total dosage of the two reagents

The values of selectivity index A, as a reflection of the physical-chemistry of the flotation system, can be well seen using the phase diagram of the dodecane-$C_{12}E_4$-water system (Fig. 88). It shows the position of different considered flotation procedures on the dodecane-$C_{12}E_4$-water phase diagram presenting the reagents concentrations and corresponding forms during the adsorption stage of the reagents on the coal surface before flotation. It shows that normal-contact flotation (NCF) is usually carried out at the water rich region of the reagents where the concentration of reagents in the system is usually less than 1%. This region is characterized by the presence of either isotropic normal micellar solutions or emulsions, which apparently are not efficient in the adsorption stage, and then in the flotation process. On the other hand, direct-contact flotation version A (DCF/A) with the anhydrous reagents, is located at the zero-water border of the phase diagram providing superior separation results at a high flotation reagents dosage. The direct-contact flotation version B (DCF/B) can be encountered at any area in the phase diagram. It also provides good results when applied in the microemulsion region using microemulsion either directly applied or formed spontaneously upon a contact of moist coal with pure anhydrous reagents. The drawback of flotation with adsorption of anhydrous reagents or microemulsion is a high consumption of the reagents. In addition, there are difficulties regarding uniform distribution of the reagents on the surface of coal.

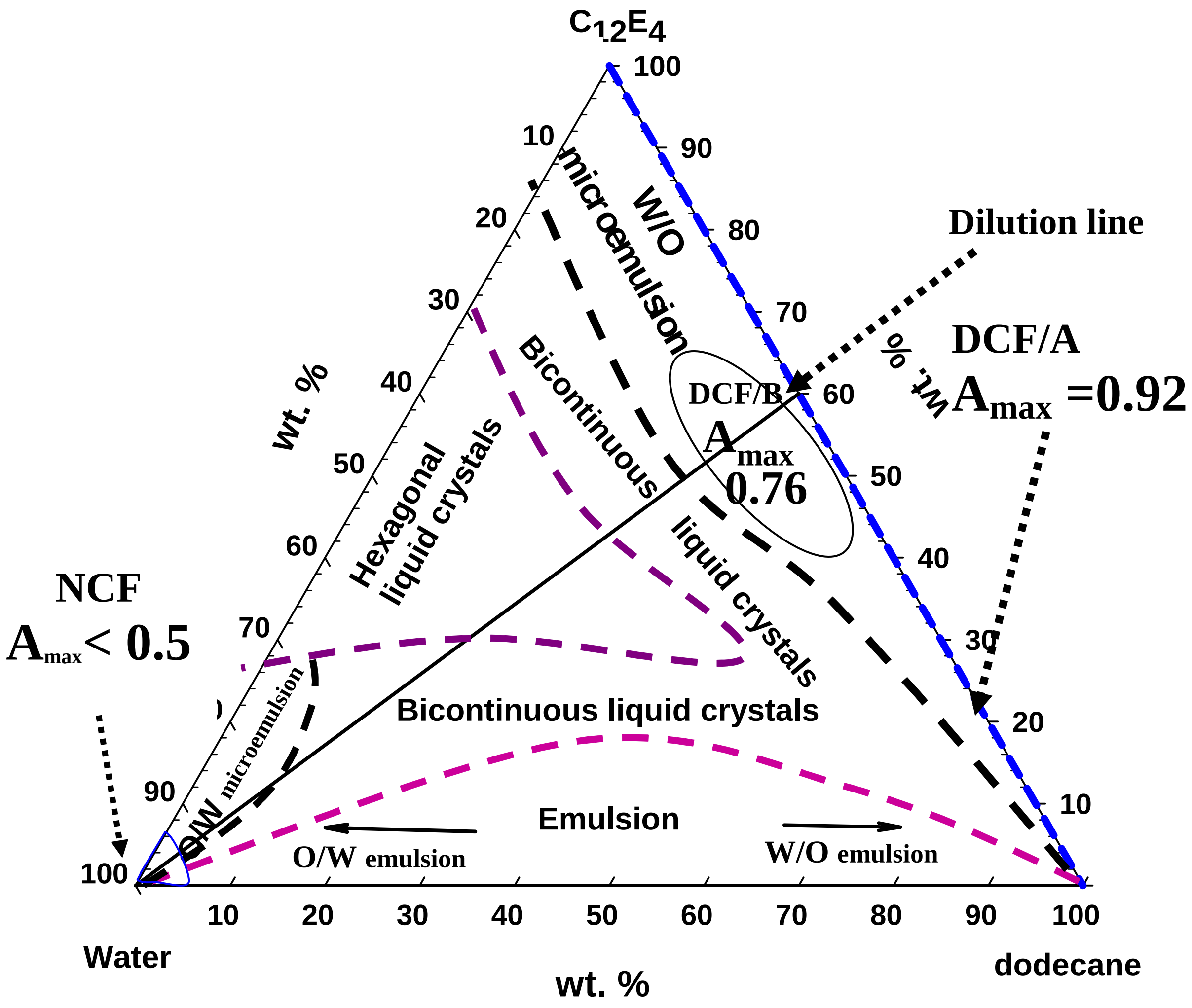


Fig. 88. The different flotation procedures related to the dodecane-$C_{12}E_4$-Water phase diagram at adsorption stage

It can be thus concluded that the DCF procedure can be used to determine the potentials of the oxidized coal flotation. Its application provides very good results which become poorer as the amount of water used with the reagents in the adsorption stage increases. Obviously, more research is needed to reduce the high reagent dosage and explore the possibility of industrial application of the direct-contact flotation procedure.

8. Summary and conclusions

Some materials are difficult-to-process and therefore they require special methods and reagents. Oxidized coal is one of such difficult-to-float materials. Different flotation tests, applying various reagents (heptane, dodecane, $C_{12}E_4$, $C_{16}E_{23}$, 1-pentanol, and α-terpineol) in different combinations (from one to three) were investigated in this thesis. Due to a great number of elements influencing a single flotation test, sometimes four (three reagents + flotation response), the thesis presented different options for graphical representation of experimental results in addition to various mathematical forms for evaluation, comparison and judging separation results plotted using the Ferestenau curve. The obtained results and their evaluations confirmed a poor flotation response of the investigated oxidized coal using the usual flotation approach. The usual flotation technique relies on contacting the coal particles with water first, followed by addition of reagents in diluted aqueous solutions, completed with a final flotation stage. Applying this approach, the best flotation results, taking into account clean coal yield, clean coal ash, and selectivity, were obtained using a 10 g/kg dosage of dodecane+$C_{12}E_4$ as mixture at the dodecane:$C_{12}E_4$ ratio of 4:1. The clean coal yield was ~60% having 2.52% ash content which points to selectivity index A of 0.463.

Much better results were obtained applying an entirely different approach. It relied on contacting the coal particles with flotation reagents in either an anhydrous or microemulsion form. The procedure provided high clean coal yield containing low ash content with a very good selectivity. For instance, a 10 g/kg dosage of the dodecane+$C_{12}E_4$ mixture, applied in the form of a microemulsion (having little amount of water), a clean coal yield of 88.4%, containing 2.48% ash with selectivity index A of 0.76, was obtained. A still better clean coal yield of ~ 95% having 2.32% ash with selectivity index A of 0.92 using 24 g/kg of the same two-reagent system (dodecane+$C_{12}E_4$) can be obtained applying the DCF/A procedure.

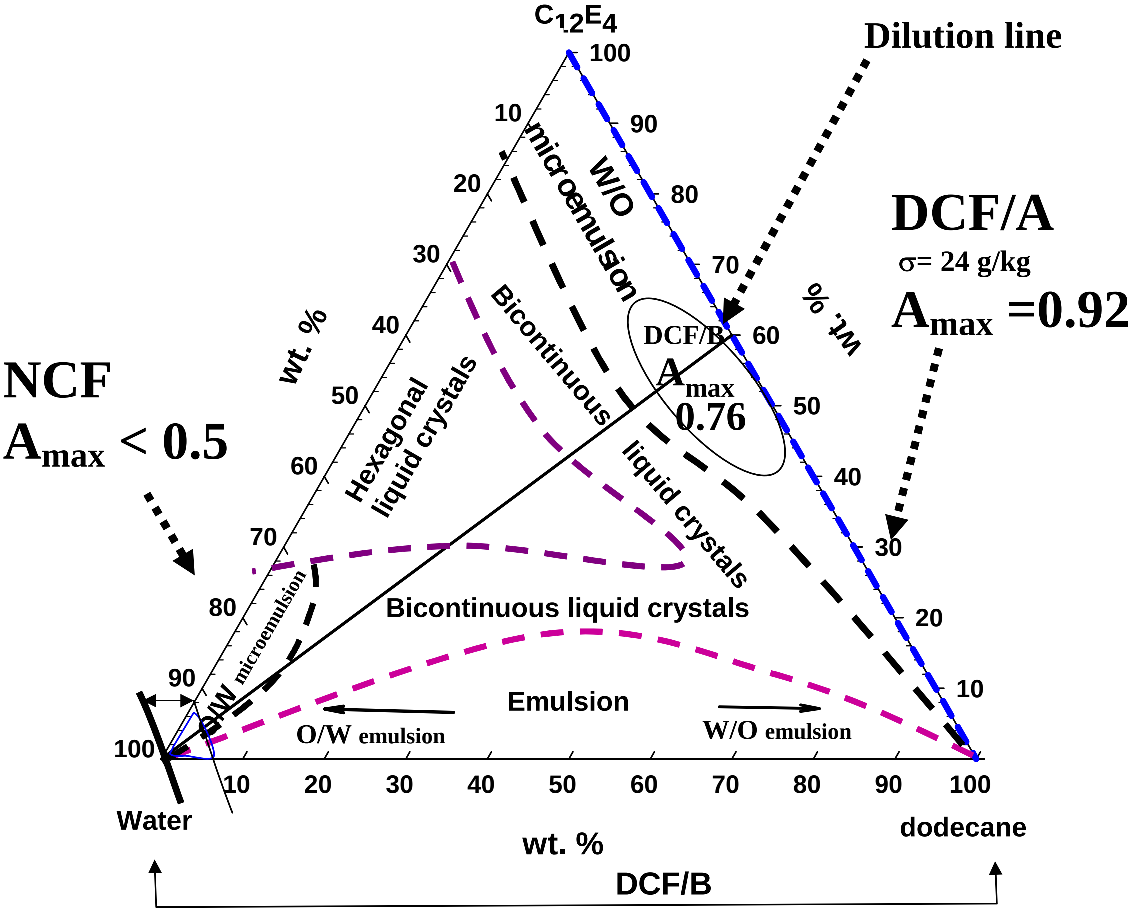


Fig. 89. Flotation results of difficult-to-float oxidized coal applying direct-contact flotation in comparison to results applying normal-contact flotation

On the basis of the results presented and discussed in this thesis and summarized in Fig. 89, the following conclusions can be drawn:

- normal-contact flotation procedure, even using special promoters as poly(oxyethelene glycol) ethers, does not provide satisfactory coal cleaning results for highly oxidized coal
- direct-contact of coal with either anhydrous flotation reagents or reagents in the form of microemulsions in the adsorption stage provided excellent coal cleaning results

- the direct-contact of anhydrous reagents with particles seems to be useful for determination of the potentials of flotation of oxidized coals
- the procedure suffer from high reagents dosage (up to 32 g/kg)
- moderate amount of moisture present in the coal plays a positive role regarding the formation with anhydrous mixture of flotation reagents of microemulsion which facilitates a good flotation of difficult-to-float coal
- more research is needed for reducing reagents consumption and testing industrial applicability of the direct-contact flotation procedure.

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Abstract

The thesis deals with upgrading materials which are difficult-to-process. It contains a literature survey covering the principles of flotation and characterization of different forms of reagents in aqueous solutions regarding their properties and application in flotation. Special approaches for upgrading difficult-to-float oxidized coals and different ways of graphical representation, evaluation, comparison, and judgment of flotation results were presented. Also, flotation of an oxidized Polish coal, using different reagents (heptane, dodecane, 1-pentanol, α-terpineol, hexadecyl tricosa(ethylene glycol) ether ($C_{16}E_{23}$), and dodecyl tetra(ethylene glycol) ether ($C_{12}E_4$)) in different combinations and concentrations, has been investigated. The applied flotation methods included the traditional flotation referred to as the normal-contact flotation (NCF) and a new approach in this thesis called the direct-contact flotation (DCF) procedure. The NCF procedure relies on addition of reagents one-by-one (version A) or as a mixture (version B) to an aqueous coal suspension followed by dilution and flotation. Using both versions of the normal-contact flotation approach, poor upgrading results were obtained in accordance with literature data on oxidized coals. The second flotation procedure, DCF, depends on contacting the dry coal sample with reagents, having no water (version A) or with a little amount of water in the form of microemulsion (version B), and then diluting the system with water. The DCF procedure showed that this approach provides a great improvement in the clean coal yield and deashing efficiency compared to that obtained applying the normal-contact flotation method. The direct-contact flotation (DCF) procedure provides information about the potentials of upgrading of oxidized coals but the reagents consumption is high (32 g/kg). The improvement of flotation results with the DCF procedure was attributed to reagents adsorption on coal surface before water, while high reagents consumption was attributed to nanoscale roughness of the coal surface. More research is needed to check the industrial application of the DCF procedure which is an example of a nanotechnology approach to solving technical problems.