Pyrolysis of casein, characterization and properties of obtained solid and liquid products

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Abstract: Have been determined the technical characteristics and elemental composition of milk casein. Pyrolysis experiments of casein carried out at different heating temperatures and determined the yields of obtained solid (biochar), liquid (tar and pyrolysis water) and gas products. A temperature around 550ºC determined as an optimal heating temperature of pyrolysis and approximately 28.33% biochar, 37.38% tar, 13.23% pyrolysis water and 20.84% gas obtained after pyrolysis. First time a biochar with higher content of nitrogen was obtained by pyrolysis of casein and determined it is elemental composition and technical specifications. The porous structure of casein biochar was characterized by mercury porosimeter and SEM analysis confirmed that casein biochar has mostly meso and macro pores. The casein tar had the elemental composition: C-66.7%, H-8.3%, N-12.1%, O-12.9% and was completely soluble in 1-methyl-2-pyrroldinone. The tar consisted mostly of moderate molecular mass components with SEC elution times between 18-26 min and an estimated mass range up to 3000-5000 mass units as well as some larger size components, possibly 3-dimentional. The property and determined chemical composition of casein tar by GC/MS analysis were an evidence for using it as a curing agent for crosslinking reactions of epoxy resins. The necessary amount of tar for curing reaction of epoxy resin was determined experimentally as a 15-20% for the stoichiometric amount of reactive epoxy groups (15-20% epoxy group content) in epoxy resin and obtained cured epoxy resin with 95% degree of crosslinking reaction. Have been suggested several curing reaction schemes of epoxy resin with amines, nitriles and phenols of the casein tar.

Keyword: *milk casein, casein pyrolysis, biochar, tar, pyrolysis water, epoxide resin, curing agent, degree of curing reaction*

INTRODUCTION

Casein, the main product of dairy industry is a food protein [1]. Besides it is relevance as a nutritional product, casein has been used for a long time in non-food applications, particularly as a binding material for plastics, man-made fibres, coatings, glues and dyes [2-4]. Uses of casein for technical applications are based on chemical modifications to the side functional groups of amino acid residues, cross linking reactions and it is good binding properties [2]. The macromolecule of casein consist of about 18-20 type of amino acid's residues and therefore it is a multifunctional biopolymer whit amorphous structure.

We have worked for long time on investigation of chemical modification and crosslinking reactions of casein as a reactable biopolymer. Have been obtained different casein glues by modification with sodium hydroxide solutions. For example have been worked out and realized technology for production of powder and liquid casein glues for wood and paper [5]. A modified with diethylenethriamine casein used as a good curing agent for synthetic epoxy resins [6]. Also have been obtained insoluble gel from sodium hydroxide solution of casein and ion exchange material from vetted casein by crosslinking with formaldehyde [7].

After all these had an idea to do thermal decomposition or pyrolysis of casein to obtain a hard, liquid and gas products. For this reason first time have been done thermogravimetric analysis of casein to determine the thermal stability characteristics such as thermostability indices ($T_{5\%}$ and $T_{50\%}$), activation energy of thermodestructive reaction of casein [8]. The thermal decomposition reaction of casein has the characteristics of first order reaction with lower activation energy $Ea= 3.87$ kcalmol^{-1}. Casein has also a lower thermal stability ($T_{5\%}=125$ºC and $T_{50\%}=355$ºC) and it means that it is thermal decomposition is very easy [8].

After these investigations have been decided to work on pyrolysis of casein and characterize obtained hard and liquid products. On the other hand we are working on pyrolysis of the basic organic raw materials such as coal [9], oil shale [10], wood [11], plastic waste [12] and some bioorganic materials including animal bone [13]. Pyrolysis, or thermal decomposition of organic materials in the absence of oxygen is of practical importance in charcoal (semi coke or hard residue) making and in the production of so-called pyrolytic oils (condensed liquid product or tar).

Unfortunately, we have found no information about the pyrolysis of other animal biomaterials including casein, except animal bone. Usually, pyrolysis hard residue of organic materials such as coal, wood, animal bone and other is a carbonized hard material with certain porosity structure. Therefore it successfully used as a adsorbing and filtering material.

So this paper contains the results on pyrolysis of casein aimed to obtain a hard residue (biochar) with high developed porosity structure and a condensed liquid product (tar) with content of unknown composition and

properties, because it never investigated before by pyrolysis.

EXPERIMENTAL

Milk casein from dairy industry is a dried solid product with yellow-wish color. The casein was crushed into pieces of 3-6 mm size and the analytical sample was prepared by powdering to a particle size < 0.2 mm in a steel mill.

Analytical sample preparation (MNS 2719:2001), proximate and ultimate analysis of casein were performed according to Mongolian National Standards MNS 656 - 79 (moisture content), MNS 652 - 79 (ash yield), MNS 654 - 79 (volatile matter yield).

The elemental composition of casein, biochar and tar were determined by micro analytical method such as 5E C2000 model CNH-analyzator.

The FTIR spectra for the biochar was obtained on a Nicolet 20 - PC FTIR spectrometer with CsI optics and DTGS detector. The KBr disc contained 0.5% finely ground biochar sample.

The small-scale pyrolysis experiments of casein samples were performed in a laboratory quarts retort (tube) which could contain air dried and powdered to a particle size < 0.2 mm 1 g of casein sample. The retort was placed in a horizontal electric tube furnace with a maximum heating temperature of 950ºC. A chrome-alumel thermocouple was immersed in the tube furnace to measure the actual heating temperature. The pyrolysis experiments have been carried out at different heating temperatures 200-700ºC with constant heating rate 20ºC/min. First of all the quarts retort with casein sample was heated for example to 600ºC with heating rate 20ºC/min and kept at 700ºC for 80 min. The retort was connected with a thermostable glass tube heated also in a tube furnace at 80ºC for collecting of tars and this tube is also connected with a air-cooled glass vessel for collecting of pyrolysis water. The glass vessel for pyrolysis water is also connected with a thin glass tube for non-condensable gases. The yields of pyrolysis products including solid residue (biochar), tar (condensed liquid product) and pyrolysis water determined by weighing, and the yield of gases by differences.

The prepapative-scale pyrolysis experiments of casein sample was performed in a laboratory vertical cylindrical retort made by stainless steel which could contain 1000 g of sample. The retort was placed in an electric furnace (model SNOL) with a maximum temperature of 950ºC. A chrome-alumel thermocouple was immersed in the casein bed to measure the actual heating temperature and an equipment for temperature control (potentiometer). The retort was connected with an air-cooled iron tube and water-cooled laboratory glass condenser and a collection vessel for the condensate of liquid product (pitch and pyrolysis water). The non-condensable gases after water-cooled condenser were left the system through a thin glass tube. The experiments were carried out to 900ºC temperature and the heating rate was 20ºC/min. The yields of products including solid residue (char), tar and pyrolysis water determined by weighing, and the yield of gases by difference.

Method for separation of tar and pyrolysis water: The liquid condensed by-product of casein pyrolysis consists from tar and pyrolysis water. They form an unmixed two layers and can be separated easily by separating glass funnel. The upper layer is tar (viscous liquid) with black-brown color and unpleasant smell. The bottom layer is pyrolysis water (non viscous liquid) with bad smell and brown color. The final cleaning of tar from the pyrolysis water residue usually use thermally treated $CaCl_2$ by mixing and separating (filtering or centrifuging).

Method for curing of epoxy resin with tar: A sample of 1 g epoxide resin of ED mark is mixing with 15-20% tar in small glass vessel and form a homogenous mixture. Have to keep this mixture for 24 h in room condition and there is no curing of epoxide resin. Therefore have to put this mixture for 2 h in oven at 120ºC and there was a curing of epoxy resin forms a hard glass like product. The cured epoxy resin will be powdered in a steel mill and 1 g of sample is packed by previously weighed filter paper and extracting with acetone on Sohxlet apparatus. After finishing of extraction the sample in filter paper have to dry at 105ºC in oven until constant weight and then will be determined the insoluble in acetone fraction (gel fraction or degree of curing reaction of epoxy resin, %).

RESULTS AND DISCUSSION

First of all the basic technical characteristics and elemental composition of casein, biochar and tar determined and the results are given in Table 1.

Table1. Analysis of casein, biochar and tar, %

Proximate and ultimate analysis	Casein	Bio-char	Tar
Moisture	8.7	4.6	-
Ash*	4.7	14.5	-
Volatile matter	78.3	11.2	100
Pyrolysis products Wt. Balance H_2O 13.3%, gas 20.9%	-	28.3	37.5
Elemental C	52.5	60.7	66.7
H	7.1	0.7	8.3
N	15.8	9.1	12.1
O+ others	24.6	29.7	12.9
H/C ratio	1.6	0.14	1.5
O/C ratio	0.19	0.37	0.14

*as determined

Pyrolysis of casein was performed in a standard laboratory quartzium retort at different heating temperatures with constant heating rate 20ºC/min and the yields of products including biochar, tar, pyrolysis water determined by weighing and the yield of uncondensed gas by differences (Figure 1). These results show that the yield of tar, pyrolysis water and gas increased with rising the temperature of pyrolysis. Only the yield of hard residue was decreased at the same time. The formed tar and hard residue were the most important products for us. Certainly the yield
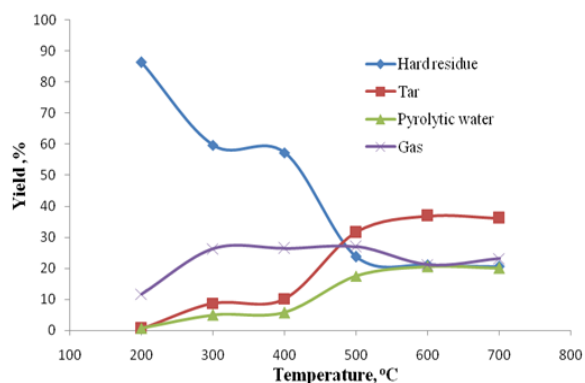
Fig. 1. The yields of pyrolysis products of casein at different temperatures.

Fig. 2. FTIR spectra of biochar of casein

of tar is lower at lower temperature, because the thermal decomposition was not enough. The optimum temperature for pyrolysis of casein was selected 550ºC, in which the yield of tar is higher. The yields of pyrolysis products of casein obtained in this condition compared with the yields of other organic materials investigated by us are given in the Table 2.
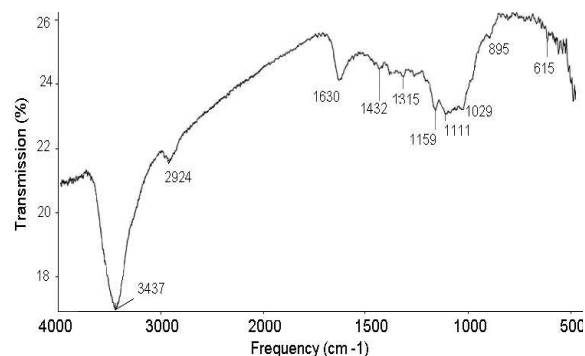
carbonization process the O/C ratio remained almost the same value. It means that O in casein had been taken part in formation of surface functional groups (–OH, >C=O, –COOH, –CO–O–CO–) of biochar. It is very interesting that nitrogen content of biochar is high, proximately 9.0%. This indicates that during pyrolysis and carbonization process nitrogen not only took part in emission of NO_x and NH_3, but also mostly

Table 2. The yields of pyrolysis products of casein compared with other organic materials and curing ability of tar for epoxy resin (%).

Materials	Hard residue	Pyrolysis water	Gas	Tar		
				Yield	Nitrogen content	Curing ability of epoxy resin
Casein	28.33	13.23	20.84	37.38	12.1	95.00
Animal bone	70.00	7.60	17.47	4.92	7.6	18.70
Oil shale	73.45	3.93	6.99	15.62	<2	No
Brown coal	68.31	7.14	15.54	8.71	<2	No
Wood waste	27.20	20.04	31.30	21.46	<2	No

Casein as a pure organic material it has the lowest ash content and highest organic matter therefore casein gives lowest yield of hard residue and the highest yield of pyrolysis liquid (tar and pyrolysis water) and gas products (Table 2). In the case of bone the yields of hard residue and pyrolysis liquid products are similar or same as for oil shale and brown coal (Table 2), because of its higher mineral matter and lower organic matter content [14]. The content of nitrogen in tars is much different depending on their origin. As a bioorganic material the casein tar has highest content of nitrogen. In the case of bone tar the content of nitrogen is lower than in casein tar. The tars of coal, oil shale and wood waste have lowest content of nitrogen, because their origin is different than casein and bone.

Characterization of pyrolysis hard residue (biochar): Table 1 shows that content of C and O in biochar increased, but content of H and N decreased in comparison with elemental dates of pure casein. These changes of elemental content depends from the carbonization process in which decomposed mostly parts of casein macromolecule with aliphatic structure and formation of biochar accompanied with cyclization or aromatization of the molecular structure of hard residue. An indication of aromatization process is the drastically decreasing of H/C ratio. During pyrolysis and

in formation of aromatization process. The biochar (casein char) was examined by Fourier transform-infrared (FTIR) spectroscopy. This analysis tool has frequently been used in investigations of surface chemistry of chars and activated carbons [10] as it provides valuable information on the chemical nature and the concentration of the surface functional groups. The FTIR spectra of biochar is presented in Figure 2. Various bonds in the spectra representing due to –OH (at 3427 cm^{-1}) aliphatic (2924 cm^{-1}), –C=O carboxyl group (1630 cm^{-1}), aromatic ring (1432 cm^{-1}), etheric –C–O–C– group (1159 cm^{-1}), aromatic –C–H (615 cm^{-1}, 500 cm^{-1}) were identified. The results of FTIR and elemental analysis show that the biochar of casein has a complex carbonized polymer material with high aromatic structure attached carbonyl and hydroxyl surface groups. The pore size distribution of casein biochar by porosimetry is shown in Figures 3 and 4. Carbonized sample of casein biochar was characterized by measuring the bulk density and the porosity (%) was calculated by formula (**1**) using the apparent (g_a=1.5567 g/cm^3) and true (g_t=2.894 g/cm^3) densities:

$$\in = (1 - g_a/g_t) \times 100 = 20\%$$

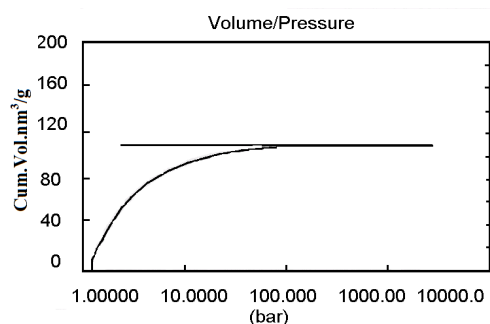From Figure 3 cumulative volume was found ~112.6

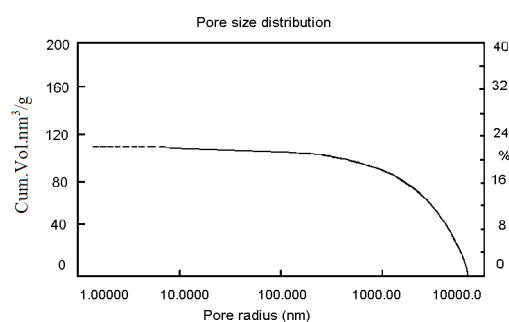Fig. 3. Relationship between volume and pressure (bar)

Fig. 4. Pore size distribution of casein biochar

mm^3/g and from Figure 4 was measured the porosity of biochar ∼ 20%, which is the same as calculated by above mentioned equation. SEM analysis of powdered sample of casein biochar is presented in Figure 5 and it also indicates the porous structure.

Pore sizes are classified in this study in accordance to the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC) [6], that is, micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm). Each type of pore plays an essential role for the adsorption property of porous materials. According to this classification of pore size the biochar of casein is characterizing with mostly meso (3.7<∅<41.7 nm) and macro pores (∅>88.04 - 6811.04
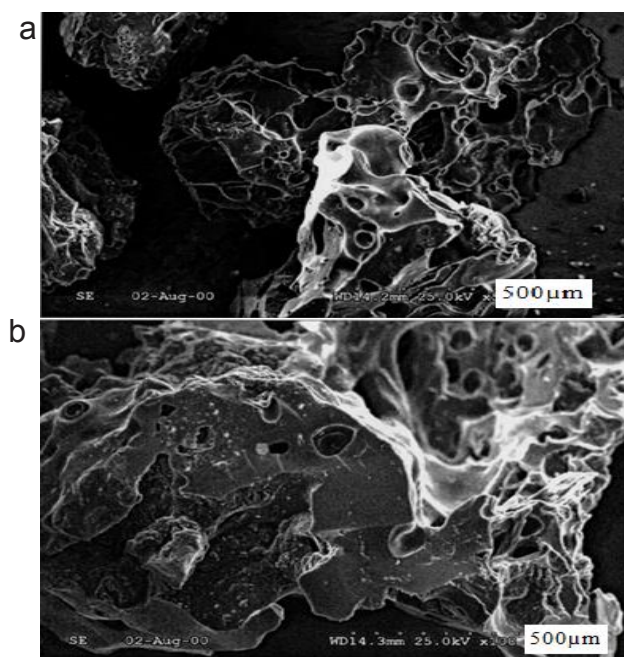

Fig. 5. SEM images of casein biochar, a. Biochar particle with porous structure.

nm) pores (Figure 5). As mentioned above the biochar is not activated, but it has a visible porous material with meso and macro pores.

The casein biochar was activated by preheated water steam at 800°C for 180 min and determined the iodine number (%) and methylene blue adsorption of initial biochar and activated biochar Table 3.

Table 3. Adsorption of casein biochar and activated casein biochar

Sample	Iodine number, %	Adsorption of methylene blue, mg/g
Casein biochar	5.39	3.6
Activated casein biochar	19.32	13.19

The results of in Table 3 show that the iodine number and methylene blue adsorption of activated biochar are almost 4 times higher than that of initial biochar.

Characterization of pyrolysis tar: The tar yield was higher than biochar yield and result of our preliminary experiment on using the tar itself as a curing agent for epoxy resin showed that it has a cross-linking ability. For this reason, we have decided to carry out detailed investigation of elemental composition, molecular mass distribution and chemical composition of the tar. The result of elemental analysis of the casein tar are given in Table 1.

If we compare the elemental composition the mass balances indicated by the result of Table 1, the carbon, hydrogen, nitrogen, oxygen content of the casein were distributed among the products in the following proportions:

C – char 32.5%, tar 47.5%, gas and water 19.7%,
H - char 2.8%, tar 43.2%, gas and water 54.0%,
N - char 17.0%, tar 30.0%, gas and water 53.0%,
O - char 34.0%, tar 19.6%, and pyrolysis water 47.0%.

These values were based on the determination of oxygen by difference and assuming the pyrolysis water was only H_2O they are the least accurate with no evidence of oxygen in the gas composition. The char can be seen as highly aromatic, probably approaching graphitic structures. The tar contained 30% of nitrogen but the H/C ratio of 1.49 indicates a mixture of aromatic and aliphatic structures. The gas and water were not analysed to determine the distribution of nitrogen.

The tar and pyrolysis water are formed in two unmixed layers and was easy to separate them in all cases of organic materials. Both smelt very bad. The casein pyrolysis tar is viscous liquid with black-brown color and it becomes thicker during keeping under room condition which was the specific property compared to the tars of other organic materials.

The chemical composition of casein pyrolysis tar as group of organic compounds is shown in Figure 6. The content of organic bases, neutral oils and phenols are higher than others. Certainly the higher content of organic bases depends on the higher nitrogen content (15.8%) of initial casein. Confirming this the tar has strong alkaline character (pH>10). The molecular mass distribution of the casein tar was examined by
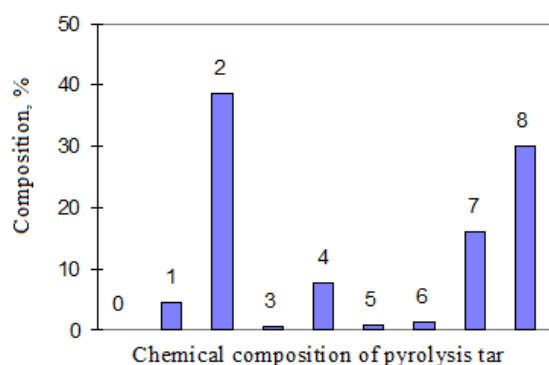
Fig. 6. The chemical composition of pyrolysis tar;
1-free carbons; 2-organic bases; 3-organic acids;
4-phenols; 5-asphaltanes; 6-paraffins; 7-neutral oils; 8-
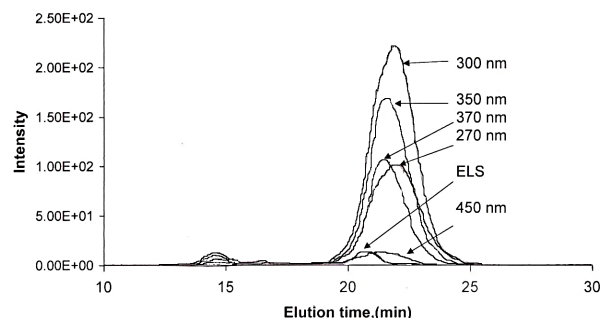preasphaltanes

Fig. 7. SEC profiles of casein pyrolysis tar on (a) Mixed-A
column. Detection by UV-A at five wavelengths 1-280 nm,
2-300 nm, 3-350 nm, 4-370 nm and 5-450 nm.

size exclusion chromatography in NMP solution at five parallel detector wavelengths; the results are presented in Figure 7.

Figure 7 shows that the major part of the sample eluted between 19 and 25 min, with a smaller peak between about 13 and 17 min. The major peak at 19-25 min corresponds to the lower molecular mass components of the tar whereas the early eluting peak at 13-17 min corresponds to material excluded from the porosity of the column, i.e. of high molecular mass or size. In terms of the calibration of the column using polystyrene standards, the mass range of the tar indicated by the calibration are, for the later peak, a range of mass from about 5400 down to less than 100 with a maximum of 200-300 mass units. The initial peak would correspond to a mass range equivalent to polystyrenes of about 15000000 down to 74000 units. Any relatively unchanged casein molecules may be expected to elute in this range.

For more detailed information about the chemical composition of tar have been carried out GC-MS analysis of casein pyrolysis tar.

Table 4. Components detected in the GC/MS of casein pyrolysis tar.

Retention time, min.	Molecular ion, m/z	Fragment ions, m/z	Molecualar formula	Name or type
0.50	41	-	C_2H_3N	Acetonitrile
0.55	55	-	C_3H_5N	Propanenitrile
0.59	68	-	$C_3H_4N_2$	1H-pyrazole
1.05	78	55	C_6H_6	Benzene
1.40	92	91	C_7H_6	Toluene
1.55	112	83	$C_6H_8O_2$	Cycloalcadione
1.59	93	43, 57, 66	C_6H_7N	Methylpyridine
2.04	81	-	C_5H_7N	Hexanenitrile
2.15	81	-	C_5H_7N	Methyl-1H-pyrrole
2.23	106	91	C_8H_{10}	Dimethylbenzene
2.34	106	91	C_8H_{10}	Dimethylbenzene
3.12	92	-	C_6H_9N	Dimethyl-1H-pyrrole
3.14	118	80	C_9H_{10}	Methylstyrene
3.42	120	91	C_9H_{12}	Propylbenzene
4.33	120	105	C_9H_{12}	Propylbenzene
	94	105	C_6H_6O	Phenol
4.49	109	91, 66	C_6H_7NO	Methoxypyridine
5.11	118	-	C_9H_{10}	Indane
6.20	108	107	C_7H_8O	Methyl phenol
7.00	108	107	C_7H_8O	Methyl phenol
7.23	122	91, 56	$C_8H_{10}O$	Anisole
7.37	117	90	C_8H_7N	Methylbenzonitrile
8.00	122	94	$C_8H_{10}O$	Ethoxybenzene
8.20	130	100, 72, 59	-	Not identified
8.54	122	107	$C_8H_{10}O$	Dimethylphenol
9.07	122	107	$C_8H_{10}O$	Dimethylphenol
9.15	128	113	C_6H_8OS	Methylmethoxythiophene
9.44	136	121, 92	$C_9H_{12}O$	Trimethylphenol
10.05	122	107	$C_8H_{10}O$	Ethylphenol
10.33	131	91	C_9H_9N	Benzenepropanenitrile
11.43	136	121	$C_9H_{12}O$	Trimethylphenol
12.38	110	82	$C_6H_6O_2$	Benzenediol
12.45	150	135, 122	$C_{10}H_{14}O$	Tetramethylphenol
12.53	117	-	C_8H_7N	Methylbenzonitrile
15.46	131	-	C_9H_9N	Methyl-1H-indole

Retention time, min.	Molecular ion, m/z	Fragment ions, m/z	Molecualar formula	Name or type
16.54	164	107	$C_{11}H_{16}O$	Alkyl phenol
17.16	198	43, 57, 71, 85	$C_{14}H_{30}$	Tetradecane
18.42	145	42, 130	$C_{10}H_{11}O$	Trimethylbenzonitrile
20.20	212	57, 71, 85	$C_{15}H_{32}$	Pentadecane
23.17	226	43, 57, 71	$C_{16}H_{34}$	Hexadecane
25.06	237	97, 110	$C_{16}H_{31}N$	Hexadecanenitrile
26.06	240	43, 57, 71	$C_{17}H_{36}$	Heptadecane
27.13	192	121, 150	$C_{13}H_{20}O$	Alkyl phenol
28.46	256	43, 57, 71, 85	$C_{16}H_{38}$	Octadecane
30.18	194	70	$C_{11}H_{18}ON_2$	Pyridine,1-acetyl-4H-pyrrolidinyl
30.38	265	251, 237, 223	$C_{18}H_{35}N$	Octadecane nitrile
31.05	154	70	-	Not identified
31.53	154	70	-	Not identified
32.40	No M+	227, 184, 71	-	Not identified
33.32	256	282, 207, 129	$C_{13}H_{12}O_2N_4$	Benzo(g)pteridine-2,4-(3H,10H)-dione, trimethyl
34.48	281	-	$C_{18}H_{35}NO$	Octadecenamide
34.56	No M+	263, 136, 122	-	Not identified
35.34	293	-	$C_{20}H_{39}N$	Eicosanenitrile
37.22	255	72, 59	$C_{16}H_{33}NO$	Hexadecanamide
41.04	No M+	281, 238, 72	-	Not identified
45.12	No M+	113, 127	-	N compound
52.11	No M+	207, 221, 281	-	Silicone
54.36	No M+	207, 221, 281	-	Silicone
56.47	No M+	207, 221, 281	-	Silicone
60.53	No M+	207, 221, 281	-	Silicone

The components tentatively identified in this way are listed in Table 4, with possible identities given against elution times; in all cases, subtracted spectra were relatively weak. Identities were from the mass spectrometer library and from the "Eight-peak index". Many of components were nitrogen-containing, with aromatic and aliphatics as well, as expected from the elemental analysis and the heated-probe mass spectra. The data in Table 4 show that there are detected more than 50 organic components of cyclic, aromatic, alkyl and alkyl-aromatic structures with different functional groups including $-H, -CH_3, -OH, -CN, >NH, -NH_2$. Also 5 components are not identified. As mentioned above the casein pyrolysis tar differs from the tar of coal, oil shale and wood with it is higher content of organic bases and thickening properties during storage time. This thickening properties indicate that there are substances sensitive to oxidation and polymerization. This property and chemical composition of tar by GC-MS analysis were an evidence for using it as a curing agent for crosslinking reactions of epoxy resins. The necessary amount of tar for curing reaction of epoxy resin was determined experimentally as a 15-20% for the stechiometric amount of epoxy resin with 15-20%

epoxy group content. The tar has good compatibility with epoxy resin and the sample was cured at 120°C for 2 h in oven. It is known that most epoxy resins have excellent solubility in acetone, but after the curing reaction with tar the sample was a solid material, more than 95% of which (the degree of curing reaction) it is insoluble in acetone. Therefore the casein pyrolysis tar can be used successfully as a good curing agent for epoxy resin, because we have achieved the same degree of curing reaction with diethylenetriamine and maleic anhydride, which are the commercial curing agents for epoxy resins. The results of GC-MS analysis of casein pyrolysis tar show that the tar is a complex or mixed curing agent with almost all these hardners as amines, phenols, acids, nitriles in it. We think the content of nitrogen (Table 2) in the tar is very important for it is curing ability for the epoxy resin. As mentioned above the content of nitrogen (12.1%) is highest in casein tar therefore it is curing ability is highest than bone tar and others. Epoxy resins known as polyepoxides are class of reactive prepolymers which contain epoxide groups (Formula 1). The epoxide groups of epoxy resins may be reacted (cross-linked) with a wide range of co-reactants (curing agents) with

Chemical formula of epoxy resin:

(1)
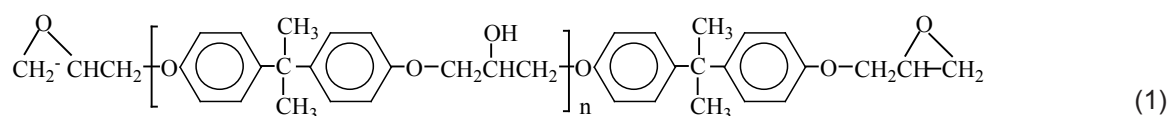
Curing reaction scheme with amines:

$$(2)$$
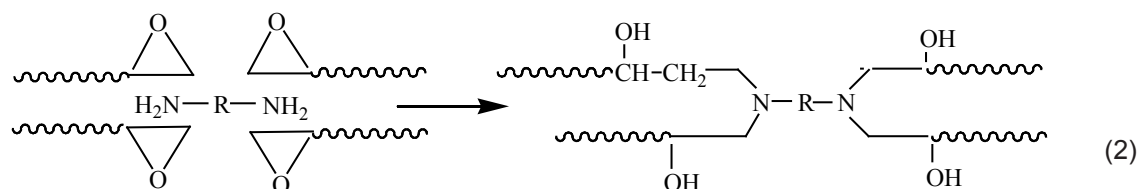
Curing reaction scheme with nitriles:

$$(3)$$
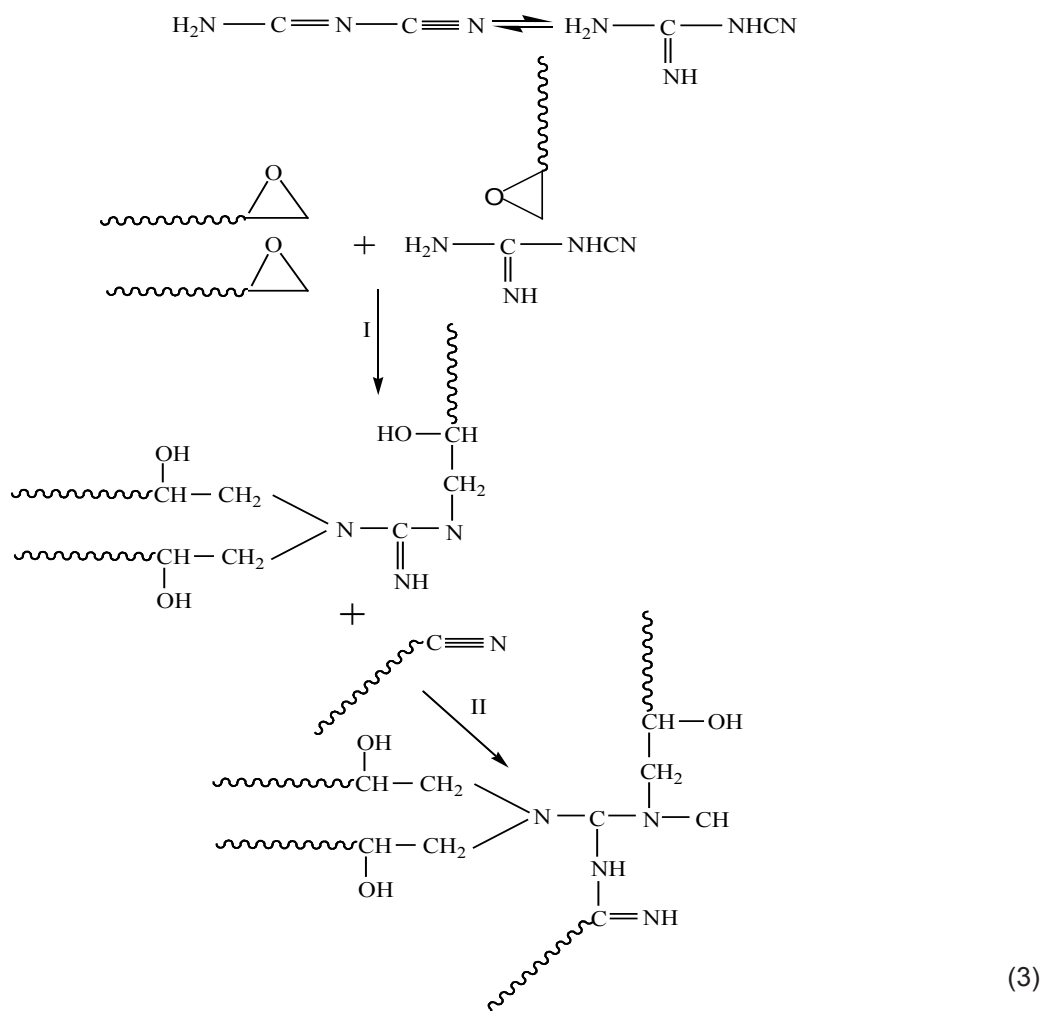
Curing reaction scheme with phenols:

$$(4)$$
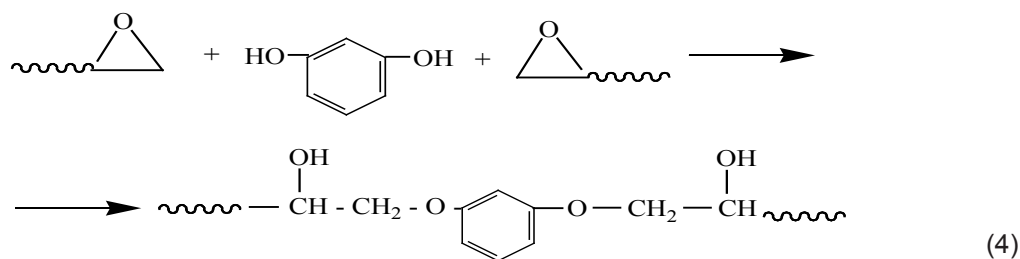
reactive H atoms in the functional groups including polyfunctional amines, acids (and acid anhydrides), phenols, alcohols, and tiols [15]. For this reason we suggest following crosslinking reaction schemes of epoxy resin with casein pyrolysis tar as a curing agent. The epoxy resin and tar are viscose liquids and completely soluble in acetone. After crosslinking reactions of epoxy resin with tar formed a glass like solid material (insoluble in acetone) with 95% degree of curing reaction, which is a confirmation of the tar to be a curing agent for epoxy resin.

CONCLUSIONS

1. Have been determined the technical characteristics and elemental composition of milk casein it`s biochar and tar after pyrolysis.

2. Pyrolysis experiments of casein carried out at different heating temperatures and determined the yields of obtained solid (biochar), liquid (tar and pyrolysis water) and gas products. A temperature around 550°C determined as an optimal heating temperature of pyrolysis and approximately 28.33% biochar, 37.38% tar, 13.23% pyrolysis water and 20.84% gas obtained after pyrolysis.

3. The yields of casein pyrolysis products have been compared with the yields of pyrolysis products of other organic raw materials including coal, oil shale, wood waste and animal bone.

4. First time biochar with higher content of nitrogen was obtained by pyrolysis of casein and determined elemental composition and technical specifications.

5. The porous structure of casein biochar was characterized by mercury porometer and SEM analysis confirmed that casein biochar has mostly meso and macro pores.

6. The casein tar had the elemental composition: C - 66.7%, H - 8.3%, N - 12.1%, O - 12.9% and was completely soluble in 1-methyl-2-pyrroldinone.The tar consisted mostly of moderate molecular mass components with SEC elution times between 18-26 min and an estimated mass range up to 3000-5000 mass units as well as some larger size components, possibly 3-dimentional.

7. The determined chemical composition of pyrolysis tar shows that the content of organic bases, neutral oils and phenols are higher than others including free carbons, organic acids, asphaltanes, paraffins, neutral oils and preasphaltanes. Certainly the higher content of organic bases depends on the higher nitrogen content (15.8%) of initial casein. Confirming this the tar has strong alkaline reactions (pH>10).

8. GC-MS mass spectrometry casein pyrolysis tar showed that there are detected more than 50 organic components of cyclic, aromatic, alkyl and alkyl-aromatic structures with different functional groups including -H, $-CH_3$, -OH, -CN, >NH, $-NH_2$. Also 5 components are not identified and the tar was very complex by GC-MS.

9. The property and chemical composition of casein tar by GC-MS analysis were an evidence for using it as a curing agent for crosslinking reactions of epoxy resins. The necessary amount of tar for curing reaction of epoxy resin was determined experimentally as a 15-20% for the stoichiometric amount of epoxy resin with 15-20% epoxy group content and obtained cured epoxy resin with 95% degree of crosslinking reaction.

10. Have been suggested several curing reaction schemes of epoxy resin with amines, nitriles and phenols of the casein tar.

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