

Experiments on the liquefaction of peat with supercritical organic solvents in a simple high-pressure/high-temperature flow reactor

Peter Köll, Jürgen Metzger & Bernd Brönstrup

with 2 figures and 5 tables

Köll, P., Metzger, J. & Brönstrup, B., 1983: Experiments on the liquefaction of peat with supercritical organic solvents in a simple high-pressure/high-temperature flow reactor. - Recent Technologies in the Use of Peat, ed. G.W. Lüttig, E. Schweizerbart'sche Verlagsbuchhandlung (Nägele u. Obermiller), Stuttgart: 143-148

Summary: From commercially available HPLC and GC equipment it is fairly simple to build a laboratory scale flow reactor which enables relatively unproblematical degradation of natural or synthetic polymers at pressures of up to 500 bar and temperatures of up to 400 °C in a stream of gas or liquid. Experiments in this apparatus on peat with ethanol/water mixtures as solvents at pressures around 150 bar and temperatures in the range of 255-285 °C showed for white peat degradation rates up to 90 %, while black peat under comparable conditions was degraded only to maximum extents of 60 %, with a much higher proportion of volatile products formed. The less volatile parts of the extracts in both cases are solid and not liquid. In the case of white peat a high proportion of the extract is water-soluble.

Zusammenfassung: Aus handelsüblichen Ausrüstungsgegenständen für die Hochdruckflüssigkeitschromatographie (HPLC) läßt sich in Verbindung mit einer geeigneten Heizeinrichtung (z.B. Gaschromatographieofen) in einfacher Weise ein Laboratoriumsreaktor zusammensetzen, der den Abbau von natürlichen und künstlichen Polymeren bei Temperaturen bis 400 °C und Drücken bis 500 bar in einem Gas- bzw. Flüssigkeitsstrom gestattet. Versuche an Torf in dieser Apparatur mit Ethanol/Wassergemischen bei Drücken um 150 bar und im Temperaturbereich 255-285 °C führten bei Weißtorf zu Abbauraten bis 90 % während Schwarztorf unter vergleichbaren Bedingungen lediglich bis zu maximal 60 % bei erheblich höherem Anteil leichtflüchtiger Produkte zersetzt werden kann. Die schwererflüchtigen Abbauprodukte sind in beiden Fällen nicht flüssig, sondern fest. Im Falle des Weißtorfes sind sie zum größeren Teil wasserlöslich.

Резюме: Опыты о сжижении торфа посредством сверхкритических органических растворов в простом реакторе высокого давления и высокой температуры. - Можно простым образом создать лабораторный реактор с использованием принятых в торговле предметов оборудования для жидкостной хроматографии под высоким давлением, а именно в сочетании с пригодной отопительной установкой (напр. аппаратура газовой хроматографии). Этот реактор позволяет осуществить деструкция естественных и искусственных по-

лимеров при температурах до 400°C и давлениях до 500 бар соответственно в газовом и жидкостном потоках. Проведившиеся посредством этого оборудования опыты на торфе с применением смесей этанола и воды при давлениях около 150 бар и в температурной области 255 - 285°C приводили в случае сфагнового торфа слабой степени разложения к величинам деструкции до 90%. Напротив, сфагновый торф высокой степени разложения в сравнимых условиях при значительно бóльшой доли легколетучих продуктов можно разрушить только до максимально 60%. Более малолетучие продукты деструкции в обоих случаях являются не жидкими, но плотными. В случае сфагнового торфа слабой степени разложения они большей частью являются растворимыми в воде.

Authors' address: Prof. Dr. P. Köll, Dr. J. Metzger & Dr. B. Brönstrup, Fachbereich Chemie - Organische Chemie - der Universität Oldenburg, Postfach 2503, D-2900 Oldenburg, FR Germany

Rising crude oil prices and the foreseeable depletion of this raw material have again led to increased global efforts to develop alternative sources for obtaining low molecular carbon compounds. In addition to a more intensive interest in the other fossil fuels bequeathed to us through the photosynthesis of times long past in the history of the earth, such as coal and lignite, there has been an obvious turn towards using constantly regenerating biomasses in particular. This is not only understandable with respect to the potential shortage of these raw materials, but also absolutely necessary in view of a lasting and well-balanced CO₂ content of the atmosphere.

Of interest are not only methods for the total gasification of the usually solid initial materials followed by the synthesis of low molecular products of value from the main products obtained - hydrogen and carbon monoxide, but also the direct conversion into liquid products. Hereby thermal, solvolytic and extractive methods with and without simultaneous and subsequent reduction respectively of the primary products (also microbial) are applied.

For the testing and application of such methods, the control of high temperatures and pressures is often necessary, which according to experience, is rather problematical in the laboratory, especially when autoclaves are not to be taken into consideration. We found that from commercially available chromatography equipment it was relatively unproblematical to build a high-temperature/high-pressure flow reactor which enabled the experimental degradation of natural and synthetic polymers of gram scale at temperatures up to 400 °C and pressures up to 500 bar in a stream of liquid or gas respectively (Köll & Metzger 1978). The apparatus (see Fig. 1) consists essentially of equipment parts for High-Pressure Liquid Chromatography (HPLC) as well as a Gas Chromatography Furnace for heating the reactor vessel (a preparative HPLC column).

Using this apparatus it is not only possible to reach high degradation temperatures, but also to produce sufficiently high pressures, which provide a degradation solvent and transport medium of sufficient density even above the critical temperature of the respective solvent. At the same time its construction as a flow apparatus brings the desired positive effect of quick removal of possibly sensitive reaction products from the degradation zone.

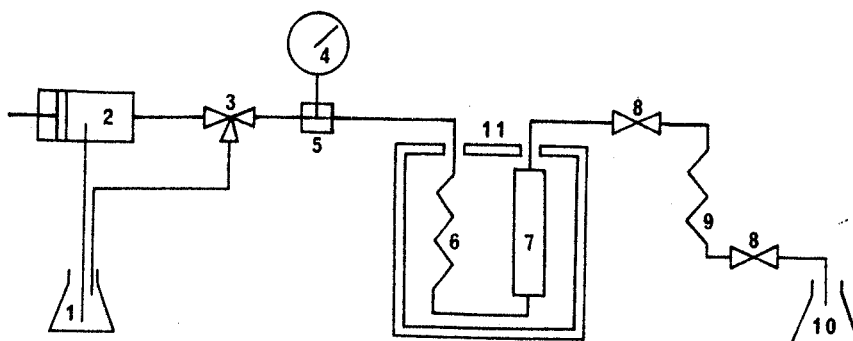


Fig. 1. Schematic set-up of the apparatus.

1 = Solvent storage jar, 2 = High-pressure pump for up to 500 bar (HPLC pump), 3 = Pressure relief valve, 4 = Pressure gauge for up to 600 bar, 5 = T-type connector, 6 = Pre-heating capillary (diameter 1.6 mm), 7 = Reactor (V = 50 ml), 8 = Valve, 9 = Heat exchanger (capillary of a 1.6 mm diameter), 10 = Receiver jar, 11 = GC furnace.

By means of this apparatus we were able to show that cellulose can be degraded with supercritical acetone at temperatures between 250 and 350 °C by 98 % and with a negligible development of gas to a water soluble syrup consisting of low molecular products. About 50 % of the extract are simple anhydrosugars. Chitin behaves in a similar manner, with, however, the one interesting difference that about 75 % of the oil obtained is not soluble in water but in organic solvents (Köll & Metzger 1978).

Extensive experiments on birch wood with a great variety of organic solvents in the supercritical range showed that mixtures of ethanol and water were particularly suited for the decomposition of this raw material which continually replaces itself (Köll, Metzger & Brönstrup 1979). At temperatures around 250 °C and water percentages from 25-55 %, not only the sensitive hemicellulose but also by far the largest proportion of lignin is dissolved, leaving behind an almost pure crystalline cellulose. However, if the water content of the ethanol is increased to 60-75 %, the cellulose, too, is attacked, causing a quantitative degradation of the wood used (see Fig. 2).

In the meantime we have extended our research to peat, another raw material which continually replaces itself. Even in 1913 Bergius reported about experiments for heating peat under pressure with water, however, without giving information to the amounts of percentages dissolved. Diakova (1941) used boiling tetralin as a solvent with the result that 80 % of the peat was converted to essentially liquid extracts. Here tetralin functions partly as a reducing agent and is oxidized into naphthalene. The conversion of peat with water in the presence of carbon monoxide under pressure at higher temperatures also functions equally reductive, as reported by two research teams in recent years (Oelert, Son & Dhin-Van 1977, Cavalier & Chornet 1977). Here maximal conversions to liquid products at an extent of over 90 % are stated.

On the basis of the good results with ethanol/water mixtures as solvents for degrading wood, we also used such solvent mixtures with white peat. The mixture which caused total degradation in the case of wood was

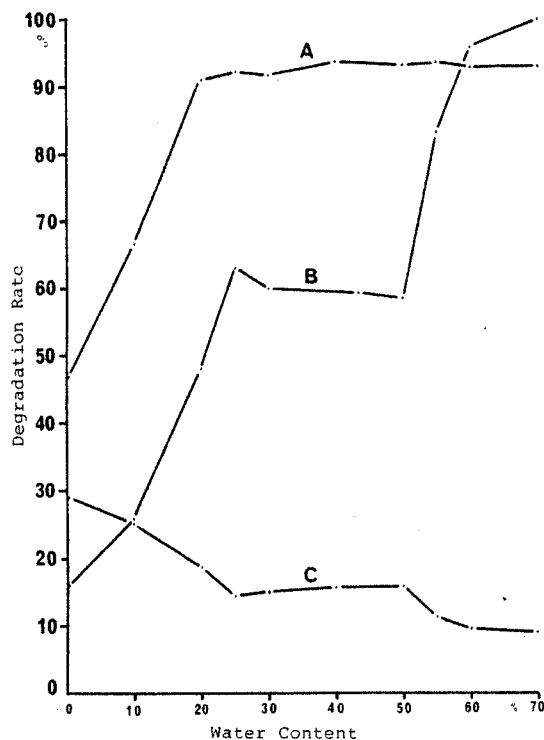


Fig. 2. Dependence of the degradation of birch wood with ethanol on the water content of the solvent under standard conditions (weight of wood sample 3 g, flow rate 1 ml/min, duration of test 1 h at 100 bar, $T = 250\text{ }^{\circ}\text{C}$).

Curve A: Weight loss of lignin
 Curve B: Weight loss of non-lignin substances
 Curve C: Quotient Q ($\times 10$):
 Curve A/Curve B

Table 1. Degradation of white peat: solvent ethanol/water 3:7 (v/v).

Test No.	Test conditions				Results			
	Temp. ($^{\circ}\text{C}$)	Flow rate (ml/min)	Pressure (bar)	Time (min)	Weight of sample (g)	Weight loss (%)	Volatiles (%)	Extract (%)
1	265	1-2	150	30	1.97	68.0	(not determined)	
2	265	7	150	60	1.77	79.8	4.2	75.6
3	265	8	150	120	2.05	89.9	4.8	85.1
4	265	7	150	30	1.42	84.3	3.6	80.7
	275			30				

the one used here. The results are shown in Table 1 (weights of samples and other data refer to the dry weight in each case).

At 265-275 $^{\circ}\text{C}$ 80-90 % of the peat can be dissolved, without larger amounts of volatile products being observed (merely 3.6-4.8 % of volatiles). The extracts obtained, however, are solid and not liquid.

Table 2 shows that the larger proportion of the extracts are water-soluble, but that a not insignificant percentage of constituents which are insoluble in both water and chloroform are present, too. This percentage can be dissolved in a diluted caustic solution, however.

Table 2. Mass balance of the extracts from test no. 2 (in parentheses test no. 3).

		Elementary analysis			
		C (%)	H (%)	N (%)	O (%)
Water-soluble part (%)	54.9 (54.1)	48.23	5.54	0.62	45.61
Chloroform-soluble part (%)	2.8 (-)	66.31	8.24	0.62	24.83
Insoluble part (%)	17.9 (31.0)	60.63	5.17	0.97	33.23

Comparing the values of the elementary analysis in Table 2 with the averages values for peat of different decomposition grades (Table 3), we find that the water-soluble part has the values of the initial peat, whereas the insoluble part has the elementary structure of strongly decomposed peat.

Table 3. Elementary analysis of peats of different decomposition grades.

Decomposition grade	C (%)	H (%)	N (%)	O (%)
Weak	48-53	5.0-6.1	0.5-1.0	40-46
Middle	56-58	5.6-6.1	0.8-1.1	34-39
Strong	59-63	5.1-6.1	0.9-1.9	31-34

If the test conditions which led to a degradation of 85 % for white peat within an hour (test no. 4, Table 1) are used with black peat, we obtain the values listed in Table 4. There is merely a weight loss of approximately 30 %, with considerable volatile products formed.

Table 4. Degradation of black peat in comparison to white peat. (Test conditions: Temp. 265 °C 30 min, 275 °C 30 min; solvent ethanol/water 3:7 v/v; flow rate 6-7 ml/min; pressure 100-200 bar).

	Weight of sample (dry weight) (g)	Weight loss (%)	Volatiles (%)	Extract (%)
Black peat	10.5	29.5	14.6	14.9
White peat	1.4	84.3	3.6	80.7

However, if the mixture ratio of ethanol to water is shifted to higher alcohol concentrations, degradation rates of up to 60 % in the case of strongly decomposed peat can even be noted (Table 5). The formation of volatile components (shown as "volatiles" in the mass balance) is, however, considerable.

Further experiments with other solvents in a supercritical state, especially those used in the extraction of coal (Gangoli & Thodos 1977) will have to show whether there are more suitable systems for decomposing black peat using the methods presented. A characterization of the extracts in the substances in question still needs to be carried out, too.

Table 5. Degradation of black peat under different test conditions.

Test No.	Temp. (°C)	Flow rate (ml/min)	Pressure (bar)	Time (min)	Weight of sample (g)	Weight loss (%)	Volatiles (%)	Extract (%)	Ratio EtOH/H ₂ O
1	255	7-8	100	60	13.6	44.7	5.8	38.9	4:6
2	255	2	100	60	2.3	44.2	13.4	30.8	4:6
3	295	3	160	120	3.5	60.4	20.7	39.7	4:6
4	275	3	150	60	4.0	52.9	12.3	40.6	6:4
5	285	3	150	600	2.9	64.7	(not determined)		4:6
6	275	6.5	150	30	10.5	29.5	14.6	14.9	3:7
	285	6.5	150	30					

References

- Bergius, M.: Die Anwendung hoher Drucke bei chemischen Vorgängen und eine Nachbildung des Entstehungsprozesses der Steinkohle. - Halle a.d.S. 1913 (cited from: Tropsch, H. & Philippovich, A.v.: Über die künstliche Inkohlung von Cellulose und Lignin in Gegenwart von Wasser. - Abh. Kennt. Kohle, 7: 84-102, 1925).
- Cavalier, J.-C. & Chornet, E.: Conversion of peat with carbon monoxide and water. - Fuel, 56: 57-64, Guildford 1977.
- Diakova, M.K.: Liquid fuel obtained by thermal solution of solids. - Compt. rend. Acad. Sci. URSS, 33: 408-411, Moscow 1941.
- Gangoli, N. & Thodos, G.: Liquid fuels and chemical feedstocks from coal by supercritical gas extraction. - Ind. Eng. Chem., Prod. Res. Dev., 16: 208-216, Washington 1977.
- Köll, P. & Metzger, J.: Thermischer Abbau von Cellulose und Chitin in überkritischem Aceton. - Angew. Chem. 90: 802-803, Angew. Chem. Int. Ed. Engl., 17: 754-755, Weinheim/Bergstr. 1978.
- Köll, P., Metzger, J. & Brönstrup, B.: Thermischer Abbau von Birkenholz mit superkritischen Gasen (organischen Lösungsmitteln) in einer Hochdruck-, Hochtemperatur-Strömungsapparatur: Die Verflüssigung von Holz und weitere Hinweise auf eine alternative Zellstoffgewinnungstechnologie. - Holzforsch., 33: 112-116, Braunschweig 1979, Druck in Berlin.
- Oelert, H.H., Dhin-Van, T. & Son, N.: Verflüssigung von Torf. - Chem.-Ing.-Techn., 49: 913, Weinheim/Bergstr. 1977.