Dry Reforming of Kraft Lignin under MWI Action

Olga V. Arapova*[a], Mark V. Tsodikov[a,b], Andrey V. Chistyakov[a,b], Gregory I. Konstantinov[a]

[a]A.V. Topchuev Institute of Petrochemical Synthesis, Leninskiy prospect, 29, Moscow, 119991, Russian Federation
[b]Gubkin Russian State University of Oil and Gas, Leninskiy prospect, 65, Moscow, 119991, Russian Federation
arapova@ips.ac.ru

In this paper presented results of efficient dry reforming of kraft lignin which was conducted over a substrate supported Fe and Ni catalysts under MWI action. The goal of current work is to give high-value aromatic alcohols and H2-rich gas. Comparing with convective heating MWI action generally provides C-H bonds cracking. Process temperature typically varied from 700 to 800°C, at 1 atm of CO_2. After 10 min of processing lignin conversion was 80-90 % depending on catalyst peculiarities. It must be noted that hydrogen yield was considerably more with the H_2/CO ratio of ~1/1 in case of MWI action comparing with convective heating that gives us an opportunity to suggest C-H bond cracking intensification under microwaves.

1. Introduction

As a kind of nonedible biomass, lignin is becoming a significant feedstock for fuels and high-value chemicals. However, lignin is the least susceptible to various chemical technologies and the usability of it only occupies approximately 2% in the conventional paper industries due to the complicated three-dimensional amorphous polymer structure. Catalytic and noncatalytic thermolysis of lignin is a viable route for producing a wide range of gases, liquids and solids that can employed for different purposes. The process is especially complex and consists of both simultaneous and successive reactions.

Last decade big attention paid to application of MWI in organic synthesis and catalysis for intensification of organic compounds conversion including biomass waste products (Chiaramonti, 2016). Recent years have seen considerable interest in lignin transformation processes stimulated by MWI. Publications of years 2012 to 2015 describe pyrolysis of mixed lignin to give hydrocarbons (Xu, 2012), glycerol and methanol (Xie, 2015), and phenols (Kim, 2013). MW-assisted catalytic processes are successfully used for depolymerization of lignin molecules (Kim, 2015).

The purpose of our work is to study the joint effect of MWI and nanosized nickel particles deposited directly on the lignin surface on the fast dry reforming of lignin to syngas.

2. Experimental

The principle scheme of laboratory MWI unit presents on Figure 1. An M-140 magnetron (1) (oscillation frequency, 2.45±0.05 GHz), was applied as a microwave radiation source; an ac power supply with a voltage of 220 V (50 Hz) was employed, and the voltage was regulated with a laboratory adjustable ratio autotransformer. The carbon sorbents with tar adsorbed in the pores were placed in a quartz flow reactor (4) which was fixed at ceramics base (3) arranged in the waveguide (2) of a microwave unit and supplied with a tungsten–rhenium thermocouple (5), which was placed in a metal casing for microwave radiation shielding. The waveguide is connected to the MWI adsorption chamber (6) (U-shaped vessel), in which due to the flow of water is realized the absorption of the residual irradiation. The correctness of the measurement of the temperature change dynamics in microwave irradiation tests was evaluated using γ-alumina as a reference substance; the results of measurements were compared with published data on the temperature measured with the aid of an IR remote sensing thermometer (Condtrol IR-T4).
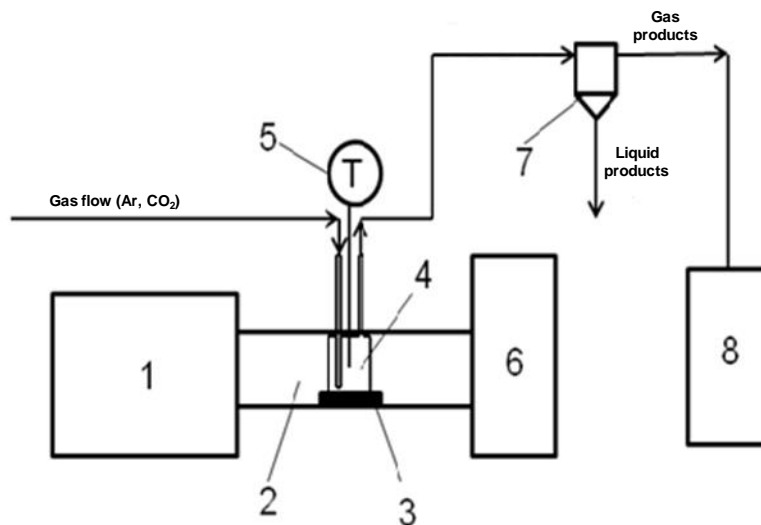
Figure 1. Principal scheme of microwave irradiation unit. 1.Magnetron, 2.Waveguide, 3.Ceramic base, 4.Quartz reactor, 5.Thermocouple, 6.MWI adsorption chamber, 7.Cooled separator, 8. GSMS unit.

Lignin (kraft lignin from Kirov Region, Russia). Composition, wt. %: C - 58.1, H - 5.4, Al - 1.2, Si - 3.1, Ca - 0.6, Fe - 0.8, Mg - 0.04, S - 1.2, N - 0.2, O - 28.9, other - 0.5 (the content of each component is less than 0.05%). GCS (gas coal sorbent): ash content - 14%, total pore volume - 1.52 cm^3/g, sorption pore volume - 0.52 cm^3/g, macropore volume - 1.00 cm^3/g. Reagents, solvents, and gases: $Ni(OAc)_2\times 4H_2O$ (Aldrich, 98%); C_2H_5OH (Sigma-Aldrich, ≥99.8%); Ar and He (special purity grade, 99.99%).

Nickel-containing lignin was prepared using impregnation. Nickel was deposited from aqueous solutions of nickel acetate $Ni(OAc)_2\times 4H_2O$. Lignin was preliminary processed under vacuum during 2 h at 1 Torr and 60^0C. The wetness was determined using conventional method before the deposition. An aqueous solution of nickel acetate containing 0, 0.2, 0.6, 1.3, 1.6, or 2.2 wt.% nickel was slowly added to 4 g of lignin up to the moment the solution volume can be entirely absorbed by the dried volume of lignin. Then the lignin sample was kept for 2 h in a closed vessel, being stirred at intervals. The wet lignin was dried in air at room temperature for 24 h and in a drying oven at 110 °C for 2 h. By the same procedure as iron system from an alcohol solution of iron acetylacetonate $Fe(AcAc)_3$ was applied to the surface of lignin and obtained samples containing 0,1% Fe. The nickel and iron content in dried lignin was determined by atomic absorption spectrometry. The procedure was reported in (Nikolaev, 2012). The chemical composition of the initial lignin was studied by atomic absorption and laser mass spectrometry on an EMAL-2 unit. The procedure was reported in (Rodicheva, 1996).

The MW-induced temperature at a specified current density was maintained by an automated magnetron switch-on controller. The power of the supplied radiation was varied by a current density controller. The residual radiation at the reaction outlet was absorbed by water. In a typical experiment, CO_2 was passed through the reactor with a sample at a 60 cm^3/min flow rate at an induced temperature of 700-750°C. For comparison with the results of MW-assisted lignin conversion, conventional reforming experiments with convective heating were carried out at 750°C and a CO_2 flow rate of 60 cm^3/min. Also, experiments on the influence of MWI on Ni-containing lignin without CO_2 were performed. For this purpose, CO_2 flow was replaced by a pure Ar flow.

Gaseous reaction products were analyzed online by gas chromatography on a Kristallux-4000M chromatograph. The hydrocarbon fraction was analyzed using a 1.5 m packed column filled with α-Al_2O_3 grains (0.5 mm) with 15% of supported squalane phase using a flame ionization detector (FID) and He as the eluent. The contents of H_2, CH_4, CO and CO_2 were determined using thermal conductivity detector (TCD) and Ar as the eluent.

In order to determine the lignin absorption capacity for MWI lignin heating dynamics was measured. If absorption of MWI was insufficient to achieve the desired temperature (above 700°C), the reactor was charged with a mechanical mixture of lignin with the GCS carbon adsorbent having, according to (Tsodikov, 2012), high dielectric loss tangent (12.72).

The conversion of lignin is determined by the following relations:

Lignin conversion based on hydrogen (%): $\alpha_{(H2)} = \frac{m_{H2in} - m_{H2res}}{m_{H2in}} \cdot 100\%$ (2), where $m_{H_{2in}}$ and $m_{H_{2res}}$ are the H_2 weights in the initial lignin and in the solid residue after reforming, respectively;

The presented lignin conversion results are an average number of the three parallel experiments. The experimental error in each series varied from 5 up to 10%.

3. Results and Discussion

Figure 2 shows the dependence of the heating dynamics of pure lignin, the carbon sorbent, and Ni-containing samples on the MWI time. Pure lignin and Ni-containing samples prepared by impregnation from a nickel acetate solution absorb MWI insufficiently for the temperature of 700-750ºC necessary for reforming to be achieved. It was ascertained in the study that on exposure to MWI, the carbon sorbent shows high heating rate to 700ºC (Figure 2, sorbent). Previously, for the carbon sorbent, a non-linear dependence of temperature rise on the current density was elucidated up to 900ºC. This provided the conclusion about plasma generation (Tsodikov, 2007). As a result, irradiation of a mechanical mixture of Ni-containing lignin, obtained from nickel acetate, with carbon sorbent rapidly resulted in the temperature of 750ºC needed for reforming, and plasma generation in the reactor was observed by sight.
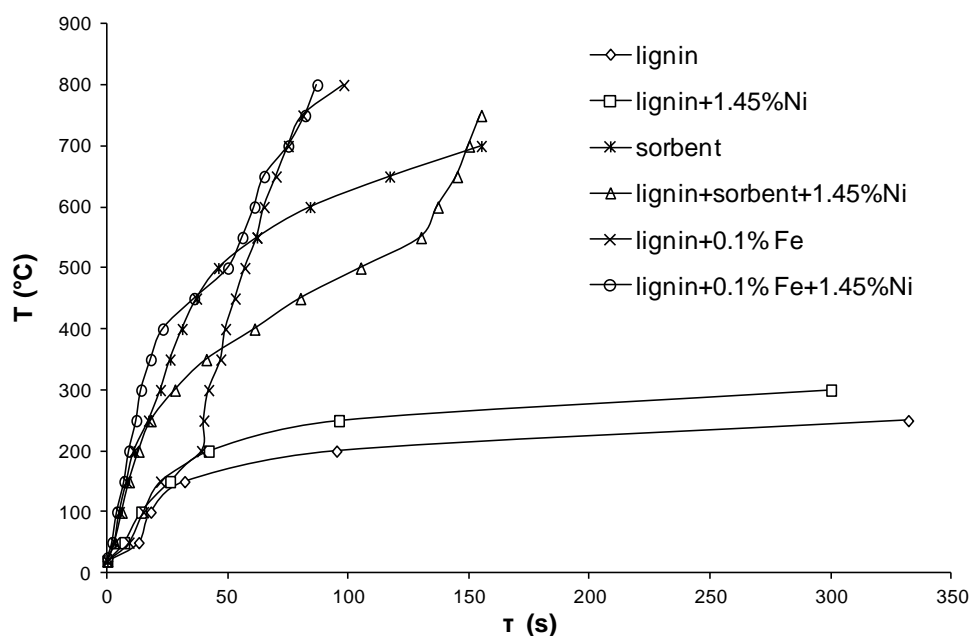

Figure 2. Microwave heating dynamics of lignin and sorbent samples.

The summary data on the composition and yield of gaseous products, lignin conversion, and yield of hydrogen and carbon monoxide for MW and convective heating of various lignin materials are given in Table 1.

We have previously found that the number of carbon materials is capable of absorbing microwave radiation, leading to the generation of plasma in the pores of the carbon material (Tsodikov, 2012). This approach has been used for the processing of carbon compounds adsorbed in the pores, including heavy oil (Tsodikov, 2016), and phosphorus compounds as models pollutant (Tsodikov, 2012). Possibility of converting of mechanical mixtures bottoms of hydrocracking process and carbonaceous materials which absorb microwave radiation was found in the development of this direction.

The approach was considered for processing of lignin, which is a complex natural polymer composed of phenylpropane units in this work. The results of the conversion of lignin under the influence of microwave radiation and conventional convective heating are presented in Table. 1.

Lignin is converted into liquid hydrocarbons, gaseous products and the solid residue in the presence of carbon material in an inert argon atmosphere. Liquid hydrocarbons consist mainly of phenyl, guaiacol and vanillin derivatives. The gaseous reaction products are hydrogen and carbon monoxide and light alkanes C_1-C_4 and C_2-C_4 olefins are presented, but their content is not more than 10 mol.%. The solid residue according to IR spectroscopy data is imperfect graphite and polyphenylene oxide structure. The yield of hydrogen is 5.9 wt.%, moreover the molar ratio of H2 / CO = 10.

Replacement of ionizing gas increases the yields of gaseous products from 13.3 to 23.5 wt.% in the case of CO_2. Hydrogen yield is increased by 0.3 wt.%, and the yield of carbon monoxide is increased by 7.7 wt.%, indicating the involvement of ionizing gas CO_2 directly into chemical interaction. Various concentrations of nickel, which is a conventional catalyst for carbon dioxide reforming of a wide range of organic substrates were applied in order to intensify the carbon dioxide reforming of lignin (to increase of hydrogen extraction degree) on the surface of the lignin.

Table 1. Main results of the lignin conversion process

№	M wt.%	Gas	oil, wt.%	gas, wt.%	char, wt.%	α(H2), %	H2 yield, wt %	CO yield, wt.%
Lignin+sorbent								
1	0	CO2	22.1	23.5	54.4	75.5	6.2	10.9
2	0	Ar	41.7	13.3	45.0	75.1	5.9	3.2
Lignin+cat+sorbent								
3	0.1 Ni	CO2	21.5	27.2	51.3	78.9	10.4	10.4
4	0.5 Ni	CO2	19	31.9	48.4	80.5	12.9	12.0
5	1.05 Ni	CO2	12.5	46.1	41.4	82.4	17.8	20.6
6	1.45 Ni	CO2	8.3	48.5	43.1	85.6	21.0	21.8
7	2.09 Ni	CO2	14.9	46.0	39.1	87.2	18.7	22.2
8	1.45 Ni	Ar	37.4	14.3	48.3	82.3	6.1	4.7
Lignin+cat								
9	0.1 Fe	CO2	3.5	54.2	42.2	87.7	19.2	24.7
10	0.1 Fe+1.45Ni	CO2	3.3	56.4	40.3	90.0	22.5	28.8
Convective heating								
11	0	CO2	38.9	19.3	41.8	83.5	2.4	10.9
12	1.5 Ni	CO2	39.8	16.3	43.9	86.6	4.2	8.0

Highest hydrogen yield equal 21 wt.% was reached by applying 1.45 wt.% nickel in CO_2 flow and in the presence of a carbon material, the molar ratio of $H_2 / CO = 1$. Note that when applied 2.09 wt.% of nickel the degree of hydrogen recovery increases by 1.6 wt.%, however the hydrogen gas yield drops to 18.7 wt.%. Probably, in the case of 2.09 wt.% nickel, the released hydrogen is partially consumed in the hydrogenation of hydrocarbon fragments of lignin, which is confirmed by the increase in oil yield. The extreme dependence of hydrogen yield on the amounts deposited nickel can be explained by the peculiarities of the morphology of the particles deposited and characteristics of their interaction with the surface groups of lignin.
Lignin, modified 1.45 wt.% of nickel, similar to unmodified lignin converted into an oil fraction when using argon gas as a medium in the presence of a carbon material, besides the quality composition of oil remains practically unchanged. The yield of hydrogen is increased slightly by 0.2 wt.%.
Comparison of the conversion of original and modified lignin in the conditions of MWI and convective heating demonstrates that the solid products yield in both cases practically unchanged, i.e. lignin processing depth is independent of the power transmission mechanism. However, a significant change of selectivity in the formation the liquid and gaseous products observed. The yield of hydrogen for the modified and the original lignin in the case of convection heating is reduced to 4.2 and 2.4 wt.%, respectively. CO yield using unmodified lignin remains constant, while it drops sharply to 8 wt.% for the modified lignin. An increase of yield of liquid organic products observed during convective heating. As in the previous examples liquid products are presented by phenyl, guaiacol, vanillyl derivatives. From these results it can be concluded that the mechanisms of formation of liquid hydrocarbons in the case of microwave irradiation and convective heating are identical. Reaction mass heating occurs under microwave stimulation, it contributes to the formation of liquid products, mainly due to cracking of the C-C bonds. As was shown in article (Tsodikov, 2016), breaking the C-H bonds of organic substrates dominates at microwave exposure that is fully confirmed in the case of lignin. Thus, the main difference of experiment conditions of convective and microwave heating effects is changing of the process selectivity, which can be directed towards the formation of liquid organic substrates

under convective heating, and toward the formation of hydrogen-containing gas in the case of microwave exposure.

Ni containing lignin conversion is a selective reaction following by syngas and solid condensation products it is reasonable to assume that terminal groups are mainly converted. Terminal groups in lignin are essentially methoxy groups [R-O-CH$_3$], where R is lignin organic mass. Equimolar yield of the syngas components usually is a result of the light aliphatic hydrocarbons C$_1$ and C$_2$ dry reforming process. This process can be described by chemical reactions which can be promoted by MWI involving methoxy groups (1-4).

$$RH[-OCH_3] \rightarrow C + H_2 + H_2O \qquad (1)$$

$$C + CO_2 \rightarrow 2CO \qquad (2)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (3)$$

$$[-O] + H_2 \rightarrow H_2O \qquad (4)$$

As a result of these reactions syngas of equimolar composition evolves. This result is observed in our experiments.

In (Chen, 2012), it was shown that the modification of various materials by nanoparticles of metals (Mo, Fe, Ni, Re) can lead to enhancement of MWI absorbtion and plasma generation. The modification of lignin by nickel particles is not lead to enhancement of absorption, but addition a small amount of iron equal 0.1 wt.% leads to a sharp increase in the absorption capacity of metal containing lignin, which expressed by the heating dynamics (Figure 2.) and its conversion in the absence of a carbon material. Modification of lignin by iron leads to reduction of liquid hydrocarbon fraction yield to 3.5% and increases the yield of the product gas, wherein the hydrogen yield is 19.2 wt.%, and the molar ratio of H2 / CO = 0.8.

In order to increase the depth of conversion of lignin and to increase the yield of hydrogen from lignin was used combined method. Lignin containing 0.5% iron additionally was modified by 1.45 wt.% of nickel. Catalytic tests showed an increase in the degree of hydrogen recovery to 90% and the yield of hydrogen to 22.5 wt.%. The yield of solid residue remained practically unchanged. In case of using Ni-Fe modified lignin observed a significant liquid products yield decrease and increasing the yield of gases. This fact indicates at different structure formation of metal centers that have varying ability to absorb microwave radiation and plasma generation directly to the active sites. Enhanced contribution of metal components in the conversion of lignin to syngas compared to its conversion without active components allows to classify the process as the plasma-catalytic.

4. Conclusion

MW-assisted dry reforming of lignin with surface-deposited nickel and iron particles results in high lignin-to-syngas conversions. The mechanism of MW-assisted reforming of Ni and Fe-containing lignin differs from the mechanism of the process induced by convective heating. It was shown that in case of MW treatment of organic compounds dominate C-H bond cracking, convective heating mainly induces lignin transformations with C-C bond cleavage, giving rise to liquid aromatics.

Analysis of the conditions for increasing the process efficiency identified a number of interesting trends concerning the formation of the nickel and iron catalysts on the surface. The yield of syngas increases for Ni and Fe containing lignin samples compared with the initial lignin both in a CO$_2$ and in a flow of Ar. Ni and Fe nanoparticles immobilized on the lignin surface contribute to catalytic activity of dry reforming and provide an opportunity for fast and selective dry reforming of lignin organic mass in plasma catalytic conditions.

Iron-containing components show significantly high ability to absorb MWI in comparison with nickel modified lignin. Addition of metal particles on the surface of lignin leads to plasma generation, and do not require using of carbon sorbents as microwave absorbents. Using lignin prepared by combined method in dry reforming under MWI can achieve high conversion of lignin to syngas. Molar ratio in gas product is H$_2$ / CO ~ 1.

References

Chen S, Si R, Taylor E, Janzen J, Chen J,2012, Synthesis of Pd/Fe3O4 hybrid nanocatalysts with controllable interface and enhanced catalytic activities for CO oxidation. J Phys Chem A, 116,12969–12976.

Chiaramonti D., Buffia M., Palmisano P., Redaelli S., 2016, Lignin-Based Advanced Biofuels: a Novel Route Towards Aviation Fuels, Chemical Engineering Transactions, 50, 109-114 DOI: 10.3303/CET1650019

Kim H.G., Park Y., 2013, Manageable conversion of lignin to phenolic chemicals using a microwave reactor in the presence of potassium hydroxide, Ind. Eng.Chem. Res. 52, 10059–10062.

Kim J.Y., Lee J.H., Park J., Kim J.K., An D., Song I.K., Choi J.W., 2015, Catalytic pyrolysisof lignin over HZSM-5 catalysts: effect of various parameters on theproduction of aromatic hydrocarbon, J. Anal. Appl. Pyrolysis 114, 273–280.

Rodicheva G.V., Orlovskii V.P., Romanova N.M., Steblevskii A.V., Sukhanova G.E., 1996, Physicochemical Investigation of Khibini Apatite and Its Comparison to Hydroxyapatite, Russ. J. Inorg. Chem. 41, 728-731.

Tsodikov M.V., Konstantinov G.I., Chistyakov A.V., Arapova O.V., Perederii M.A., 2016, Utilization of petroleum residues under microwave irradiation, Chem. Eng. J.292, 315–320.

Tsodikov M.V., Perederii M.A., Chistyakov A.V., Konstantinov G.I., Kadiev Kh.M., Khadzhiev S.N., 2012, High Speed Exhaustive Utilization of Petroleum Residues and Pollutants, Solid Fuel Chem. 46, 121–127.

Tsodikov M.V., Perederiy M.A., Karaceva M.S., Maximov Y.V., Suzdalev I.P., Gurko A.A., Zhevago N.K., 2007, Formation of iron-containing catalysts on carbon carriers under the influence of microwave radiation, Nanotechnol. Russ. 1, 153-161

Tsodikov M.V., Perederii M.A,. Chistyakov A.V, Konstantinov G.I., Martynov B.I., 2012, Degradation of Organophosphorus Compounds Adsorbed in Carbon Sorbent Pores, Solid Fuel Chem 1, 39–47.

Xie J., Qi J., Hse C., Shupe T.F., 2015, Optimization for microwave-assisted directliquefaction of bamboo residue in glycerol/methanol mixtures, J. For. Res. 26, 261–265.

Xu J., Jiang J., Hse C., Shupe T.F., 2012, Renewable chemical feedstocks fromintegrated liquefaction processing of lignocellulosic materials using microwave energy, Green Chem. 14, 2821.