Characterizing Polymeric Methylene Diphenyl Diisocyanate Reactions with Wood: 1. High-Resolution Solution-State NMR Spectroscopy

Daniel J. Yelle
U.S. Forest Products Laboratory, USDA Forest Service, Madison, Wisconsin

Joseph E. Jakes
Materials Science Program, University of Wisconsin-Madison, U.S. Forest Products Laboratory, Madison, Wisconsin

John Ralph
Dep. of Biochemistry (Enzyme Institute) and D.O.E. Great Lakes Bioenergy Research Center, University of Wisconsin-Madison, Madison, Wisconsin

Charles R. Frihart
U.S. Forest Products Laboratory, USDA Forest Service, Madison, Wisconsin

Abstract

Solution-state nuclear magnetic resonance spectroscopy (NMR) is a powerful tool for unambiguously determining the existence or absence of covalent bonds between wood components and adhesives. Finely ground wood cell-wall material dissolves in a solvent system containing dimethylsulfoxide-d_6 and N-methyl–imidazole-d_6, keeping wood component polymers intact and in a near-native state. Two-dimensional (2D) NMR experiments, using ^{13}C-^{1}H one-bond heteronuclear single-quantum coherence on non-derivatized cell-wall material from loblolly pine, reveal details about the major cell-wall polymer structures. This technique can detect new covalent bond formation between cell-wall polymers and wood adhesives. A monofunctional model of polymeric methylene diphenyl diisocyanate (pMDI) and also neat pMDI were reacted without catalysts with loblolly pine matchsticks under moisture-controlled conditions to chemically modify the wood cell-wall polymers. The modified matchsticks were ball-milled, dissolved, and characterized via 2D NMR experiments. Results showed that high concentrations of the pMDI model reacted to form carbamate linkages with mannan and lignin sidechain units at 160°C. However, the pMDI-reacted matchsticks showed no reactivity at 160°C, thus indicating that the mechanism of durable bond formation between wood and pMDI is not controlled by urethane formation.

Introduction

Covalent bonds between an adhesive and wood are believed to improve bond durability. Given that 1) aryl isocyanates are well known to readily react with alcohols to form carbamates (Saunders and Slocombe 1948), 2) wood contains a substantial amount of naturally hydroxylated polymers, and 3) isocyanates have been thought to infiltrate the cell wall (Marcinko et al. 1994), we postulated that the phenyl isocyanate-based adhesives were the most likely of the wood adhesives to form covalent bonds to the wood polymers, and thus selected them for our studies.

Isocyanates undergo several competitive reactions. Polyurea is formed from the copolymerization reaction of the diisocyanate with water and leads to polymerization of the adhesive in the bondline. Wendler and Frazier (1996) found that when the wood is dry (moisture content < 5%), polymeric methylene diphenyl diisocyanate (pMDI) reacts to form urethane and low molecular weight biuret structures. As the wood moisture increased (> 5%), they found that polyurea formation dominated, thus optimizing penetration into wood. Urethane (i.e., covalent bond) formation with wood polymer hydroxyls may provide a secondary "anchoring" mechanism within the cell wall at moisture contents > 5% (Wendler and Frazier 1996) (the molecular weight of the pMDI used in this reference was much higher than what is used in industry).

The difficulties in distinguishing between urea, biuret, and urethane structures in wood-pMDI bondlines are

caused by their structural similarities. Zhou and Frazier (2001) prepared pMDI with a double-isotopic label (i.e., ^{15}N and ^{13}C) in the isocyanate to enhance detection of urethane formation in the cured wood-pMDI bondline using solid-state NMR spectroscopy. However, urethane and polyurea signals displayed substantial overlap in the acquired spectra; therefore, covalent bonds couldn't be identified unambiguously (Zhou and Frazier 2001).

Recently, a solution-state NMR spectroscopic method was developed to allow for a better determination of isocyanate reactivity with wood. High-resolution solution-state NMR spectroscopy can detect covalent bond formation between wood polymers and adhesives. Using non-degradative wood dissolution (Lu and Ralph 2003), finely ground wood cell walls dissolve in a solvent system containing dimethylsulfoxide-d_6 and N-methylimidazole-d_6, keeping wood polymers in non-derivatized state (Yelle et al. 2008). Two-dimensional (2D) NMR experiments, using ^{13}C–^{1}H one-bond heteronuclear single-quantum correlation (HSQC) spectroscopy on whole cell walls reveal the major cell-wall polymers. Using this approach we have examined the reaction of loblolly pine with phenyl isocyanate (PI) and 4-benzylphenyl isocyanate (BPI) using a swelling solvent and conditions similar to industrial oriented strandboard (OSB) processes and found that β-aryl ether and phenylcoumaran primary hydroxyls (both found in lignin) predominantly reacted when NCO:OH (NCO:OH means the number of moles of isocyanate groups to the number of moles of accessible wood cell-wall polymer hydroxyl groups) molar ratios were 1:1 at a moisture content ≅0%. However, covalent bonds were not detected under a NCO:OH molar ratio of 1:1 where moisture content was ≥ 5% (Yelle 2009). In this study, we further investigate the reactivity between wood cell-wall polymers and phenyl isocyanate and pMDI adhesive to determine the exact site(s) of carbamate/urethane formation (if reaction occurs) without using a swelling solvent. Specifically, we 1) characterize non-catalyzed reactions between PI and loblolly pine matchsticks; 2) characterize non-catalyzed reactions between pMDI adhesive and loblolly pine matchsticks; and 3) assign new peaks in the ^{13}C–^{1}H spectra of reaction products between the isocyanate and wood cell-wall polymer hydroxyls using a previously developed wood carbamate NMR database.

Materials and Methods

Loblolly pine matchstick-size specimens were all latewood and were cut from the same growth ring having the dimensions 1 × 1 × 30 mm. The matchsticks were then equilibrated to ≅ 0 and 14% moisture contents using chambers housed with phosphorus pentoxide and saturated sodium chloride, respectively. Phenyl isocyanate (PI, dried over 3Å molecular sieves), dibutyltin dilaurate (DBTDL), and dimethylsulfoxide-d_6 were obtained from Aldrich Chemical Company (Milwaukee, WI). N-methylimidazole-d_6 was synthesized using previously described methods (Yelle et al. 2008). The pMDI adhesive was Lupranate M20SB (BASF Corporation, Mount Olive, NJ), formulated for OSB.

The matchsticks (five per treatment) were removed from their respective chambers and immediately weighed using a Mettler-Toledo (Mettler-Toledo Inc., Columbus, OH) model XS105 analytical balance to 0.01 mg accuracy. Then, the matchsticks were transferred to a 50 mL round-bottom flask (Teflon joints), purged with nitrogen, immersed with either PI or pMDI to achieve a NCO:OH molar ratio ≅ 2:1 with or without DBTDL using the conditions described in **Table 1**. For samples reacted with PI or pMDI at 160°C, the reaction flask was ramped from ambient to 160°C over a period of ≅30 min. using an oil bath and held for 2 h. After treatment, the matchsticks were removed from the flask and dried in a vacuum oven (with a cold trap between the oven and pump) at 50°C and ~10 mbar overnight to remove excess PI. The dry weights of the treated matchsticks were then obtained to 0.01-mg accuracy, and weight-percent gains (WPG) were calculated for each treatment. Two of the matchsticks per treatment were subjected to nano-indentation, and those results will be presented in Part 2 of this study. The remaining three matchsticks per treatment (≅100 mg) were collectively ball-milled using a Retsch (Retsch, Inc., Newtown, PA) PM100 planetary ball-mill with ZrO_2 balls and vessel, dissolved in dimethylsulfoxide-d_6 and N-methylimidazole-d_6 (4:1, v/v) directly into a 5-mm NMR tube, as previously described (Yelle et al. 2008).

Solution-state NMR spectroscopy was acquired at 50°C on a Bruker DMX-500 instrument equipped with a cryogenically cooled 5-mm TXI $^{1}H/^{13}C/^{15}N$ gradient probe with inverse geometry. The central solvent peak was used as an internal reference (δ_C = 39.5 ppm, δ_H = 2.49 ppm). HSQC experiments (pulse program = hsqcetgpsi) had the following parameters: sweep width, 9.0 to 1.0 ppm in F_2 using 1602 data points (acquisition time, 200 ms) and 150 to 10 ppm in F_1 using 600 increments (F_1 "acquisition time," 17.04 ms). The number of scans was 64 with a 1-s interscan delay and the total acquisition time was 13 h 39 min. Processing used typical matched Gaussian apodization in F_2 and squared cosine-bell in F_1.

Results and Discussion

Previous work reacted PI and BPI with microtomed loblolly pine in the swelling solvent N,N-dimethylacetamide without catalysts (Yelle 2009). The swelling solvent effectively increased the polymer free-volume in the lignin-hemicellulose matrix to allow the PI and BPI greater access to lignin and galactoglucomannan hydroxyls. Interestingly and somewhat expectedly, both the PI and BPI showed reactive preference towards lignin sidechains.

In the current study, PI and pMDI were reacted neat with loblolly pine. The goal of each sample treatment was as follows: Sample 1, an ambient conditions control; Sample 2, to promote PI reaction with bound-water in the cell wall, thus forming diphenyl urea and/or biuret structures; Sample 3, a heat-treated (160 °C) control; Sample 4, to obtain phenyl carbamylated wood polymers and PI reaction with bound-water in the cell wall, thus forming diphenyl urea and/or biuret structures; Sample 5, to obtain only phenyl carbamylated wood polymers through the use of dry wood; Sample 6, to mimic industrial OSB

Table 1. ~ *Conditions used for loblolly pine matchstick treatments.*

Sample no.	NCO type	NCO:OH†	% M.C.‡	Temp. (°C)	Catalyst§	WPG¶
1	–	–	14	25	–	–
2	PI	2:1	14	25	DBTDL	62.2
3	–	–	14	160	–	–14.2
4	PI	2:1	14	160	none	87.7
5	PI	2:1	0	160	none	104.4
6	pMDI	2:1	14	160	none	45.1

†Molar ratio of isocyanate groups to wood hydroxyl groups (Yelle 2009).

‡Percent moisture content in the wood.

§Dibutyltin dilaurate was added at 0.2% by weight of dry wood.

¶Weight-percent gain was calculated on an oven-dry basis.

conditions. ^{13}C–^{1}H HSQC spectra of the reacted loblolly pine (without prior extraction or isolation steps) depict the whole cell-wall of each sample treatment.

Figures 1-1 through **1-6** contain the HSQC spectra showing the aliphatic region of the whole cell walls. **Figure 2** shows the structures depicted in the HSQC spectra. In the spectra, the contours of interest are from β–aryl ether units (A), phenylcoumaran units (B), β-D-mannopyranosyl units (Man), and their respective reacted moieties (C-A, C-B, or C-Man). Other contours are not assigned here. **Figure 1-1** shows the native state of the cell wall at ambient conditions, where unreacted lignin sidechains and mannan chemical shifts match those of lignin model compounds (Ralph et al. 2004) and Norway spruce β-D-mannopyranosyl units (Hannuksela and du Penhoat 2004). When the matchsticks (14% moisture content) were treated with PI at 25°C with DBTDL as a catalyst (**Fig. 1-2**), no change in the chemical shifts for all cell-wall polymers was seen, thus indicating no reaction. However, the WPG of Sample 2 showed a weight increase of 62%. Therefore, diphenyl urea most likely was able to partially fill or bulk the cell lumina along with the possibility of diphenyl urea forming in the cell-wall matrix. **Figure 1-3** shows the cell wall after heat-treating at 160°C, thus showing that the temperature regime used for the isocyanate reactions does not affect the chemical shifts of the native-state polymers. Sample 3 showed a weight loss equivalent to 14.2%, meaning that the heat treatment efficiently removed the moisture in the cell wall, confirming that the matchsticks were indeed equilibrated to 14% moisture content. When the matchsticks (14% moisture content) were treated with PI at 160βC (**Fig. 1-4**), the Man2 (3.82/70.1 ppm), Man3 (3.71/72.5 ppm), and Man6 (3.70/60.8 ppm) positions of β-D-mannopyranosyl units were partially reacted to give C-Man2 (5.50/70.0 ppm), C-Man3 (5.16/73.5 ppm), and C-Man6 (4.5-4.1/63.0 ppm) contours with slight reactivity with the β–aryl ether and phenylcoumaran gamma hydroxyl depicted by the small C-Aβ contour (4.60/81.3 ppm) and C-Bγ contour (4.40/65.2 ppm); the C-Aγ contour is masked by the C-Man6 contour. Two other new contours were found as well at 4.7 to 4.5/72.5 ppm and 4.7 to 4.4/74.0 ppm (**Fig. 1-4** and **1-5**) that are currently unknown reacted hemicelluloses. The WPG of 88% for Sample 4 must then be partially attributable to the carbamylation of the mannan; diphenyl urea and biuret structures must be present to the extent where all available water molecules were reacted and the excess isocyanate was then available to react with the mannan. When the matchsticks (≅0% moisture content) were treated with PI at 160°C (**Fig. 1-5**), similar results to Sample 4 were found; C-Man2, C-Man3, and C-Man6 contours are depicted with small C-Aβ and C-Bγ contours. The two new contours seen in **Fig. 1-4** are also seen in **Fig. 1-5**. The WPG of Sample 5 was 104%, indicating that carbamylation of the mannan and β–aryl ether was either more effective under dry conditions or more of the lumina were filled When the matchsticks (14% moisture content) were treated with pMDI at 160°C (**Fig. 1-6**), the spectra showed identical chemical shifts to that of **Fig. 1-1** and **1-3** (Samples 1 and 3). Therefore, no reaction with the cell wall was found with the pMDI adhesive under the conditions employed here, which are similar conditions of temperature and moisture content to that of industrial OSB fabrication. These results are consistent with the previous study where loblolly pine was hot-pressed in an automated bond evaluation system (ABES) at 160°C and moisture content at 5 and 14% (Yelle 2009). The WPG of Sample 6 was 45%, indicating that the pMDI was able to enter the lumina; however it is not clear from this study whether or not pMDI entered the cell-wall matrix.

Conclusions

Although PI reacts with some cell-wall polymers at 14% moisture content and to a greater extent under dry conditions, pMDI did not react with the cell-wall polymers to any measurable degree under conditions mimicking OSB fabrication. These results show that pMDI adhesives, under typical OSB bonding conditions, do not form urethanes with wood. This suggests pMDI adhesives bond to wood through physical mechanisms such as hydrogen bonding, van Der Waals forces, or interpenetrating polymer networks (IPN) (Frazier and Ni 1998). The pMDI may have the capacity to enter into the lignin/hemicellulose matrix. At the molecular scale, the polyurea has the ability to form intermolecular hydrogen bonds between wood hydroxyl protons and the urea carbonyl oxygen as well as the wood hydroxyl oxygen and the urea amine proton. To investigate the

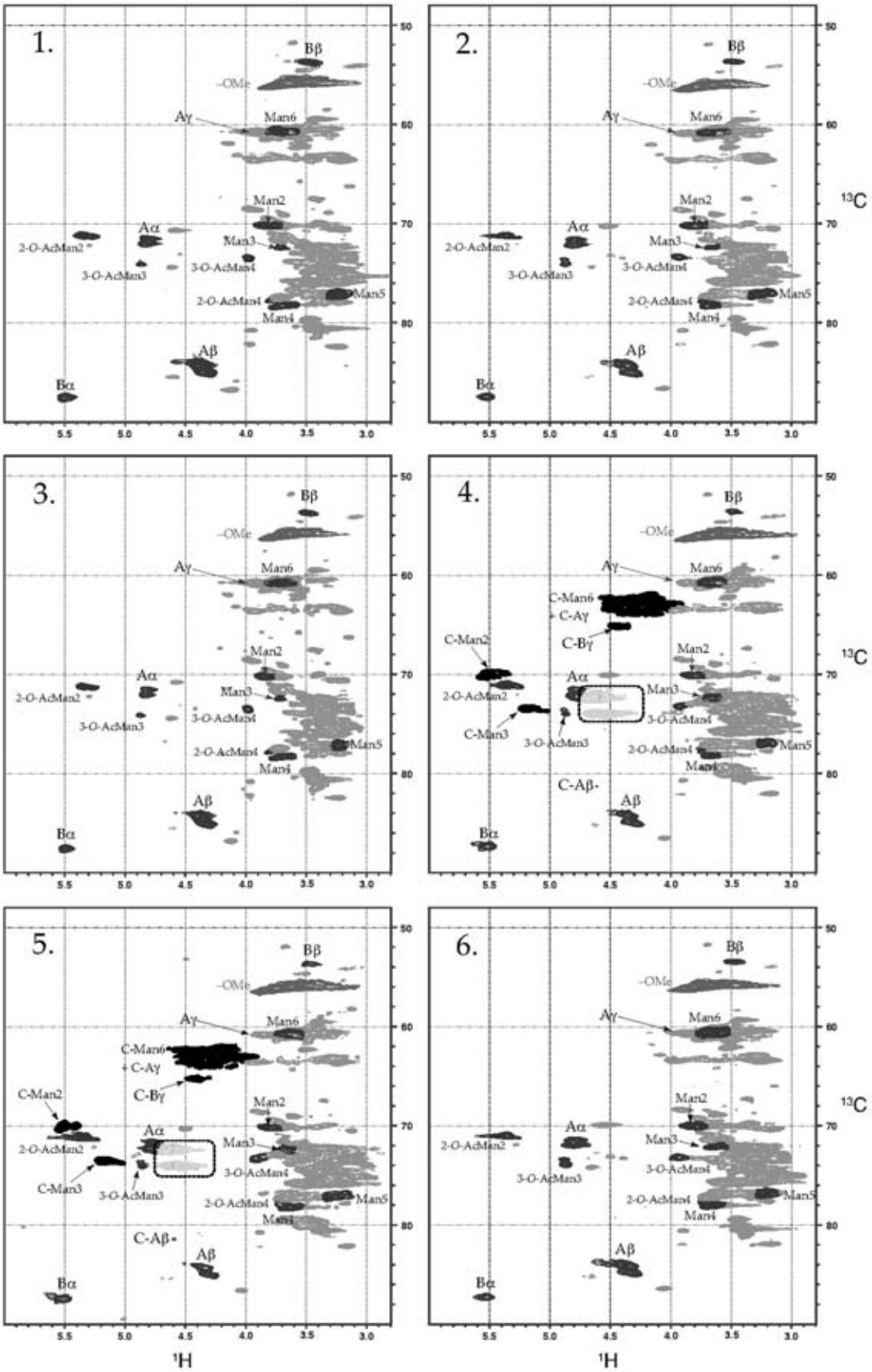

Figure 1. ~ *HSQC ^{13}C-^{1}H correlation spectra of the six treated matchstick samples where the numbers at the top-left of each spectrum correspond to the samples in Table 1. The spectra show the aliphatic region where lignin sidechain and polysaccharide correlations are found. C-Man, C-A, and C-B in the spectra denote a carbamylated structure (i.e., reaction with isocyanate). In spectra 4 and 5, the dotted box indicates currently unknown reacted hemicelluloses.*

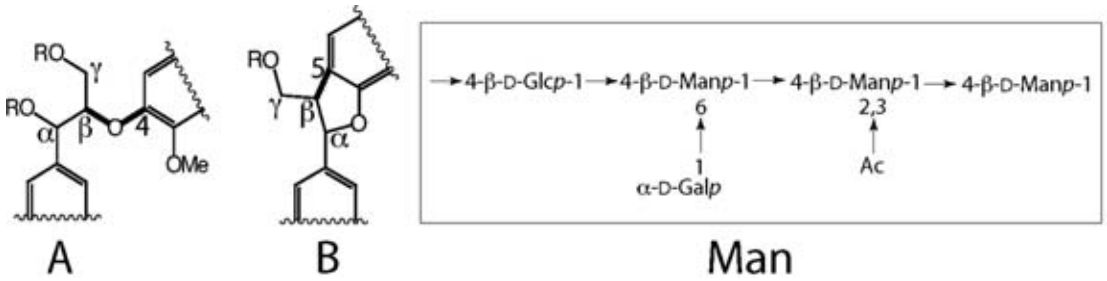

Figure 2. ~ *A key to the structures shown in Figure 1: A, β-aryl ether units; B, phenylcoumaran units; Man, β-D-mannopyranosyl units.*

nanomechanics of each treated matchstick sample, nano-indentation experiments have been performed to obtain the elastic modulus and hardness creep behavior of the S2 layer and middle lamella, which is described in Part 2 of this study. The next phase of this research will explore the characteristics of the physical bonding mechanisms between pMDI and the wood cell wall.

Literature Cited

Frazier, C.E., and J.W. Ni. 1998. On the occurrence of network interpenetration in the wood-isocyanate adhesive interphase. Int. J. Adhes. Adhes. 18:81–87.

Hannuksela, T., and C.H. du Penhoat. 2004. NMR structural determination of dissolved O-acetylated galactoglucomannan isolated from spruce thermomechanical pulp. Carbohyd. Res. 339:301–312.

Lu, F., and J. Ralph 2003. Non-degradative dissolution and acetylation of ball-milled plant cell walls: High-resolution solution-state NMR. Plant J. 35:535–544.

Marcinko, J.J., W.H. Newman, and C. Phanopoulos. 1994. The nature of the MDI/wood bond. pp. 286–293. *In* Second Pacific Rim Bio-Based Composites Symposium, Vancouver, Canada. The University of British Columbia, Vancouver, B.C.

Ralph, S.A., J. Ralph, and L.L. Landucci. 2004. NMR database of lignin and cell wall model compounds. Available at: http://ars.usda.gov/Services/docs.htm?docid=10491; verified 2 May 2010.

Saunders, J.H., and R.J. Slocombe. 1948. The chemistry of organic isocyanates. Chem. Rev. 43:203–218.

Wendler, S.L., and C.E. Frazier. 1996. Effect of moisture content on the isocyanate/wood adhesive bondline by N-15 CP/MAS NMR. J. Appl. Polym. Sci. 61:775–782.

Yelle, D.J. 2009. A Solution-State NMR Approach to Elucidating pMDI-Wood Bonding Mechanisms in Loblolly Pine. Ph.D. dissertation. In Forestry/Chemistry, University of Wisconsin, Madison, WI. 169 pp.

Yelle, D.J., J. Ralph, and C.R. Frihart. 2008. Characterization of non-derivatized plant cell walls using high-resolution solution-state NMR spectroscopy. Magn. Reson. Chem. 46:508–517.

Zhou, X.B., and C.E. Frazier. 2001. Double labeled isocyanate resins for the solid-state NMR detection of urethane linkages to wood. Int. J. Adhes. Adhes. 21:259–264.

Wood Adhesives 2009 / edited by Charles R. Frihart, Chiristopher G. Hunt, and Robert J. Moon.
Madison, WI : Forest Products Society, c2010. 1 CD-ROM.
ISBN 978-1-892529-57-2. FPS Proceedings no. 7216-09.