Simulation of Gas Production Mechanisms in Shear Deformation of Medium-Rank Coal
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ABSTRACT: The discovery of mechanochemical action provides a theoretical basis for revealing gas production from coal under stress degradation. The research on gas production in such a manner is conducive to revealing mechanisms of coal and gas outburst and excess coalbed methane (CBM). By selecting a model of a macromolecular structure of Given medium-rank coal, its structure was optimized based on molecular mechanics, molecular dynamics, and quantum chemistry, and the six optimized models were constructed into a coal polymer cell. The coal polymer cell was loaded to shear deformation through large-scale atomic/molecular massively parallel simulator (LAMMPS) software. The Given model was optimized by quantum chemistry software Gaussian and the frequency was calculated to obtain the bond strength and average local ionization energy (ALIE). The following understanding was reached: under shear, bridge bonds of a ring structure, and large π-bonds are subjected to shear and tensile action, and atoms (atomic clusters) in the outermost region of coal macromolecules tend to be sheared by surrounding molecules. The shear action shortens a molecular chain of medium-rank coal with a cross-linked structure and promotes the evolution of the coal macromolecular structure. The shear action can lead to the formation of free radicals, such as H* and CO from macromolecules of medium-rank coal, thus producing many small gas molecules, such as H2 and CO. Moreover, the shear action can not only break chemical bonds but also can produce new chemical bonds. The research on gas production mechanisms under shear deformation of medium-rank coal provides a certain reference for studying mechanochemistry.

1. INTRODUCTION
Mechanochemical phenomena have long since been discovered: until the end of the 19th century, when Matthew Carey Lea proved that Ag and HgCl2 can produce Cl2 by mechanical grinding, while heating HgCl2 can only sublimate powder, mechanochemistry was established as an independent branch of chemistry.1 In 1919, Wilhelm Ostwald proposed the concept of mechanochemistry.2 Force directly changes chemical bonds, leading to reactions,3 which reduces obstacles to, and accelerates, chemical reactions.4 Stress can even change reaction pathways by changing reaction barriers. Different from the way that stress affects the reaction,5 heating can increase the energy of reactants and make more reactants cross the reaction barriers, but heating cannot reduce the reaction barriers. The latest research shows that force can directly act on molecular structures to make them change chemically, that is, mechanochemical action.6–8

White explained that the metamorphism of coal in the eastern USA is mainly caused by structural stress.9,10 This is particularly true for unconventional coalification near thrust faults, typically shown in ① Rocky Mountains;11 ② Cordillera Mountains and Kandersteg Region in south-eastern Canada,12 and ③ the Swiss Alps.13 Graphitization, the end stage of coalification, may occur on carbon-rich faults.14,15 In the research into graphitization, it is generally believed that shear stress plays an important role in this process,16,17 which may promote the gradual alignment of basic structural units18,19 and reduce the activation energy of coal graphitization.20 Graphitization can occur in shear tests at a temperature as low as 873.15 K, while it is realized at above 2273.15 K in simple heating tests. Using electron paramagnetic resonance (EPR), researchers have found that more free radicals are induced by bond breaking under stress/mechanical force.21 The results of Fourier transform infrared (FTIR) spectroscopy...
and carbon-13 nuclear magnetic resonance ($^{13}$C NMR) show that tectonically deformed coal (TDC) has lower aliphatic carbon atoms and higher aromatic carbon atoms compared with the adjacent undeformed coal. TDC and undeformed coal are sampled from contiguous areas, so they show the same thermal evolution and differences in influences of stress. The effects of stress on TDC are summarized as stress degradation and stress condensation, indicating that stress can promote the early evolution of coal.

It has also been reported that coal can produce gas molecules under the action of external force. As early as 1966, Juntgen and Karweil found that, when bituminous coal is ground at 473.15 to 573.15 K, gases, such as CO, H$_2$, CO$_2$, and CH$_4$, can be generated. A team led by professor Hou Quanlin also detected CO gas through creep experiments at a low temperature and high pressure on high-rank coal and studied gas-production processes and mechanisms during coal deformation through quantum mechanical calculation. The external force on coal can be divided into tensile, compressive, and shear actions. Combined with the previous research results, it is found that compression cannot chemically change the macromolecular structure of coal, while tension can degrade its macromolecules into relatively small molecular fragments. Therefore, it is considered that only shearing action can cause the coal macromolecular structure to produce small gas molecules. Using the widely recognized medium-rank coal to represent macromolecular structures of Given coal, the corresponding coal polymer model was constructed based on a molecular dynamics simulation and studied by loading the coal to shear deformation. The aim is to reveal mechanisms of gas production in the deformation of the macromolecular structure of coal.

2. SIMULATION AND CALCULATION METHODS

2.1. Construction and Optimization of Coal Polymer Cells. The macromolecular structure of Given medium-rank coal, with chemical formula C$_{102}$H$_{84}$O$_{10}$N$_2$, was mainly dominated by cross-linked structures. It included structures, such as benzene rings, naphthalene rings, common five-membered carbon rings, common six-membered carbon rings, common seven-membered carbon rings, oxygen-containing functional groups, nitrogen-containing functional groups, and methyl groups. To understand the broken chemical bonds more intuitively, the line mode was used in the macromolecular structure model of the coal, and part atomic-number information was added to select the best angle for output, as shown in Figure 1.

The macromolecular structure of Given coal was plotted by Materials Studio (Accelrys Inc.) software, and six macromolecular structures of Given coal were optimized and loaded to assemble polymer cells. The specific optimization details are demonstrated in the method provided by Yang, as shown in Figure 2.

2.2. Simulation of the Shear Process in Coal Polymer Cells. The optimized polymer model of Given coal was transformed into a data format recognized by LAMMPS. The three-dimensional periodic boundary conditions and ReaxFF force fields were used. The energy of the model was minimized by sd and cg methods, and the temperature was kept at 298 K by the temp/rescale method in the NVE system. The coal polymer model was simulated by applying shear in the XY-, XZ-, and YZ-directions at the real strain rate of $1.5 \times 10^{-3}$, and the calculation was carried out in 4000 steps.
3. RESULTS

3.1. Chemical Bonds Broken (Generated) in Coal Macromolecules under the Shearing of Medium-Rank Coal. By sorting the bond.reaxc file output by LAMMPS, it is found that there are 40 broken chemical bonds in total, and six chemical bonds are newly generated through observation combined with the Ovito visualization process. Statistics pertaining to each broken chemical bond and the numbers thereof are listed in Table 1 and those pertaining to newly generated chemical bonds in Table 2.

Based on data in Table 1 and connection of chemical bonds in the macromolecular structure of the Given coal (Figure 1), more broken chemical bonds are located at the connection of each part, such as chemical bonds C18–C27, C19–C24, C37–C39, C39–C40, C39–C99, C41–C42, C41–C47, C42–C98, C43–C44, C80–C81, C94–C99, C96–C97, and C97–C98. The others are at the periphery of molecules, such as C50–H141, C76–H166, C50–H141, O112–H198, and O93–H183. There are also various types of broken chemical bonds, including various chemical bonds containing H (hydroxyl, methyl, and methylene), C–C single bonds, and large π-bonds.

The generated chemical bonds comprise five-membered rings formed by breaking one bond in six-membered rings and bonds formed by the combination of free radicals, such as N24–C80 and C96–O112.

3.2. Bond Breaking Order of Coal Macromolecules under Shear. Under shear, the chemical bonds of each coal macromolecule are broken in different orders. By taking the XY-direction as an example, the shearing action causes the Y-axis to deform in the X-direction. The broken chemical bonds of six molecules and their order are summarized in Table 3.

As demonstrated in Table 3, under shear, the overall trend is as follows: C–H and O–H bonds are most easily broken and then large conjugate π-bonds and C–C cross-linked bonds are broken alternately. The C–H and O–H bonds are mostly located in atoms (atomic group) in the periphery of basic structural units of coal macromolecules. The C–H bonds are mainly located on methylene, such as C76–H166 and C58–H153 connected by bridge bonds and methyl (C50–H141).

### Table 1. Statistical Table of Broken Chemical Bonds and Times About 6 Given Coal Macromolecules During Shearing

| chemical bonds | bond breaking times | chemical bonds breaking times | chemical bonds | bond breaking times |
|----------------|---------------------|-----------------------------|----------------|---------------------|
| C17–C18 | 1                    | C43–C44                   | 2                | C81–C86          |
| C18–C27 | 2                    | C44–C45                   | 1                | C81–H170         |
| C19–N24 | 3                    | C50–H141                  | 2                | C82–C87          |
| C25–C28 | 1                    | C55–H144                  | 1                | C87–H175         |
| C26–C27 | 1                    | C58–H153                  | 1                | C94–C95          |
| C26–C34 | 1                    | C61–C62                   | 1                | C94–C99          |
| C29–C30 | 1                    | C64–C65                   | 1                | C95–C103         |
| C36–C42 | 1                    | C65–H155                  | 1                | C96–C97          |
| C37–C39 | 2                    | C67–C68                   | 1                | C97–C98          |
| C39–C40 | 2                    | C72–C73                   | 1                | O112–H198        |
| C39–C99 | 2                    | C73–H159                  | 1                | O1–H115          |
| C41–C42 | 2                    | C76–H166                  | 1                | O93–H183         |
| C41–C47 | 2                    | C80–C81                   | 3                |                   |
| C42–C98 | 2                    | C80–H169                  | 1                |                   |

### Table 2. Statistical Table of New Chemical Bonds and Times About 6 Given Coal Macromolecules During Shearing

| chemical bonds | C17–C19 | N24–C80 | C40–C47 | C94–C98 | C96–C103 | C96–O112 |
|----------------|---------|---------|---------|---------|----------|----------|
| forming bond   | 1       | 1       | 1       | 1       | 1        | 1        |

The O–H bonds are mainly found on hydroxyl, such as O93–H183 and O112–H198. Furthermore, C–C bonds mostly reside on bridge bonds (C37–C39, C39–C40, C39–C99, C41–C42, and C42–C98), chemical bonds on seven-membered rings (C41–C47 and C43–C44), and large π-bonds (C19–N24, C94–C99, and C96–C97).

3.3. Products of Given Medium-Rank Coal under Shearing Action. The macromolecular structure model of coal is mainly dominated by a cross-linked ring structure and only contains some structures, such as ketone bonds, hydroxy, methyl, and bridge-bound methylene. Under shear, only a small number of H* free radicals are separated from the macromolecular structure, and a ring-opening reaction tends to occur (Figure 3). These H* free radicals combine with each other to form small stable H2 molecules, and CO is produced through some ring-opening reactions.

It can be seen from Table 3 that H atoms are separated first, followed by CO under the shear action of medium-rank coal. Therefore, H2 and CO are successively produced from this medium-rank coal under shear. According to the statistical results, the numbers of H* and CO are 19 and one, and two H free radicals can form a H2 molecule. The amount of gas produced can be calculated by molecular weight, as shown in Formula 1.
atom. Molecule no. 6 underwent ring-opening reaction, shedding the H atom, and H atom transfer from O93
underwent the complex ring-opening and binding reaction, shedding atom transfer from O93
Molecule no. 1 underwent a ring-opening reaction, shedding
Figure 3. Small molecules formed by shearing about Given coal. (a) Molecule no. 1 underwent a ring-opening reaction, shedding \( ^{*} \)CO, H atom transfer from O93–H183 and O112–H198. (b) Molecule no. 3 underwent the complex ring-opening and binding reaction, shedding the H atom, and H atom transfer from O93–H183 and O112–H198. (c) Molecule no. 6 underwent ring-opening reaction, shedding the H atom.

| bonds broken sequence | no. 1 | no. 2 | no. 3 | no. 4 | no. 5 | no. 6 |
|-----------------------|-------|-------|-------|-------|-------|-------|
| 1                     | O112–H198 | C19–N24 | O112–H198 | O93–H183 | C58–H153 | O112–H198 |
| 2                     | O93–H183 | C81–H170 | C73–H159 | C19–N24 | O93–H183 | C65–H155 |
| 3                     | C96–C97 | C18–C27 | C93–H183 | C17–C18 | O112–H198 | C43–C44 |
| 4                     | C43–C44 | C80–C81 | C42–C98 | C17 + C19 | C19–N24 | C55–H144 |
| 5                     | C50–H141 | C82–C87 | C39–C40 | C37–C39 | C64–C65 | O1–H115 |
| 6                     | C41–C42 | C80 + N24 | C94–C99 | C80–C81 | C41–C42 | C41–C47 |
| 7                     | C94–C95 | C42–C98 | C94 + C98 | C36–C42 | C18–C27 | C87–H175 |
| 8                     | C39–C99 | C19–C99 | C96–C97 | C26–C27 | C19–C40 | C97–C98 |
| 9                     | C97–C98 | C96–C97 | C96 + O112 | C50–H141 | C80–H169 | C49–C94 |
| 10                    | C72–C73 | C95–C103 | C61–C62 | C44–C45 | C26–C28 | C29–C30 |
| 11                    | C80–C81 | C96 + C103 | C81–C86 | C26–C34 | C41–C47 | C40 + C47 |
| 12                    |       |       | C41–C47 | C40 + C47 | C37–C39 | C87–H175 |
| 13                    |       |       | C41–C47 | C37–C39 | C67–C68 | C87–H175 |
| 14                    |       |       | C41–C47 | C67–C68 |       |       |
| 15                    |       |       |       |       |       |       |
| 16                    |       |       |       |       |       |       |

\( ^{+} \) represents new forming bonds.

\[
G = \frac{nM_f \times 22.4 \times 10^{-3}}{M_i \times M_f \times 10^{-6}} \tag{1}
\]

where \( G \) represents the production (m\(^3\)/t) of \( f \) gas (\( f \) represents the type of gas, including H\(_2\), CO); \( n \) denotes the amount of gas \( f \) (the amount of H\(_2\) is \( n/2 \)); \( M_i \) and \( M_f \) denote the mass fractions (g/mol) of gas \( f \) and coal polymer, respectively.

By substituting 19/2 and 1 into formula 1, the production of H\(_2\) and CO from this Given coal polymer under shear was found to have reached 23.71 and 2.50 m\(^3\)/t, respectively.

4. DISCUSSION

H atoms are produced by breaking of chemical bonds containing H atoms under shear. H atoms on methyl (C50–H141 bonds of nos 1 and 4 molecules), methylene (C73–H159 and C76–H166 bonds of no. 3 molecule; C58–H153 and C80–H169 of no. 5 molecule; C55–H144, C65–H155, and C87–H175 of no. 6 molecule), methylidyne (C81–H170 bonds of no. 2 molecule), and hydroxyl (O93–H183 on nos 1, 3, 4, and 5 molecules; O112–H198 on nos 1, 3, 5, and 6 molecules and O1–H115 on no. 6 molecule) can be separated under shear.

\(^{*} \)CO is generated by separating H atoms on O112–H198 hydroxyl of no. 1 molecule, breaking large \( \pi \)-bonds C96–C97 on benzene rings, and finally breaking C97–C98 bonds. The ring-opening reaction mainly happens to two categories of chemical bonds, namely, rings formed by common single rings (double rings) and rings formed by large \( \pi \)-bonds. They are mainly concentrated in three large areas: ① C17–C18, C18–C27, C19–N24, C25–C28, C26–C27, C26–C34, and C29–C30; ② C36–C42, C37–C39, C39–C40, C39–C99, C41–C42, C41–C47, C42–C98, C43–C44, C44–C45, C94–C95, C94–C99, C95–C103, C96–C97, and C97–C98; and ③ C61–C62, C64–C65, C67–C68, C72–C73, C80–C81, C81–C86, and C82–C87. The breaking of bonds propagates from both ends to the middle.

4.1. Effects of Position of Chemical Bonds in Molecules on Breaking of Chemical Bonds under the Shear Action.

The spatial distribution of each Given coal macromolecule in the polymer is different. The atoms (atomic clusters) on the periphery of molecules are the first to contact, and the relative movement between the molecules will produce the shearing
action. In this case, the chemical bonds (chemical bonds on the periphery of molecules) connected by atoms (atomic groups) at the shearing site are subjected to shearing action, and the connected parts are stretched by the shearing point. Therefore, tensile action occurs at the earliest and affects each molecule in the shear process. Coal molecules, being soft molecules, are stretched to some extent under tensile action. When chemical bonds rotate clockwise around the point of action in the direction of the applied shear (the positive X-direction), the rotation angle is between 0 and 90° (or between 270 and 360°) so that chemical bonds are easily broken under tensile action. When shear is applied at shear sites to a certain extent, chemical bond threats are broken. For the macromolecular structure of coal, there are obvious cross-linked structures. The cross-linked structure contains bridge bonds of low strength and lies in the middle of molecules, making any direct effect difficult to realize, but an indirect effect on the surrounding chemical bonds arises, therefore, the cross-linked part is protected. Therefore, the ring-opening reaction of the macromolecular structure involves tensile breaking. The chemical bonds in the long-chain ring structure break from both ends and failure thereof gradually develop to the middle. The shear action is manifested in two ways: chemical bonds connected to atomic groups in the outermost regions of molecules are broken under shear and H atoms are mainly separated. They include O1−H115 (hydroxyl), O93−H183 (hydroxyl), O112−H198 (hydroxyl), C50−H141 (methyl), C55−H144 (methylene), C58−H153 (methylene), C65−H155 (methylene), C73−H159 (methylene), C76−H166 (methylene), C80−H169 (methylene), C81−H170 (methylene), and C87−H175 (methylene). Chemical bonds in the middle of the structure are readily subjected to tensile action, leading to tensile breaking. The chemical bonds mainly include C−C and C−N bonds, such as C17−C18 (a large π-bond), C19−N24 (a large pyridine π-bond), C26−C27 (a large π-bond), C26−C34 (a carbon−carbon single bond), C36−C42 (a carbon−carbon single bond), C37−C39 (a carbon−carbon single bond), C39−C40 (a carbon−carbon single bond), C39−C99 (a carbon−carbon single bond), C41−C42 (a carbon−carbon single bond), C41−C47 (a carbon−carbon double bond), C42−C98 (a carbon−carbon single bond), C43−C44 (a carbon−carbon single bond), C44−C45 (a carbon−carbon single bond), C64−C65 (a carbon−carbon single bond), C80−C81 (a carbon−carbon single bond), C82−C87 (a carbon−carbon single bond), and C94−C99 (a large π-bond). The position of chemical bonds in the whole molecule determines whether chemical bonds are subjected to tensile action or shear action in the shear process and ultimately determines the manner in which the chemical bonds break.

Under either tensile or shear action, the angle between a chemical bond and the shear direction constantly changes throughout the shear process. To determine the change of the angle between the chemical bond and the shear direction under shear, the coordinates of all atoms are output using a step length of 50 steps in LAMMPS software. The broken chemical bonds of no. 1 molecule in this coal polymer are not only present in significant quantity but are also of various types (separated H atoms and CO). The angle between the broken chemical bond and the X-direction is calculated by taking the data pertaining to no. 1 molecule as an example, as shown in Figure 4.

![Figure 4. Angle between the broken chemical bonds and shear direction about no. 1 molecule in Given coal polymer varies with the shear process.](https://doi.org/10.1021/acsomega.1c04739)
A smaller absolute value of $\Delta R$ suggests that the bond length of the chemical bond changes little as the bond rotates by 1° and the chemical bond is mainly subjected to shearing action; a larger absolute value of $\Delta R$ implies that the bond length of the chemical bond changes significantly per degree angle of rotation and the chemical bond is mainly subjected to tensile action. $\Delta R$ is calculated from the final two data points before breaking of no. 1 molecule and the key statistical data are listed in Table 4.

In accordance with $\Delta R$ data in Table 4, chemical bonds are broken under shearing action when $|\Delta R| \leq 0.100$ and under tensile action when $|\Delta R| > 0.100$. While breaking, when the data points selected show that the length of chemical bonds is two to three times the initial length, the chemical bonds are considered to be completely broken.

As shown in Figure 4, for the ring structure, the broken chemical bonds are subjected to shearing action, under the influences of which the angle ($\theta$) between the chemical bond and the shear direction gradually increases. Such a process is evinced by changes in the bond angle of chemical bonds, corresponding to the rotation of chemical bonds, while the bond length changes slightly. As the angle ($\theta$) between the chemical bond and the shear direction begins to exceed 90°, significant strain energy is accumulated and the force changes from rotation to tension. With the increase of the distance between atoms, chemical bonds are rapidly broken, and the action mechanisms are shown in Figure 5. Atoms shown in red are subjected to the shear action, and the force can be decomposed into compression along the direction of the bond length (due to the relationship between the bond length and bond energy, the compressibility of bond length is very limited), and rotation occurs perpendicular to the direction of the bond length. When the chemical bonds rotate more than 90°, the force on those atoms shown in red can be decomposed into a stretching action along the bond length direction and a rotation perpendicular to the bond length direction. When the angle between the chemical bond and the shear action exceeds 30° while breaking, $|\Delta R| \leq 0.100$, such as for chemical bonds O112–H198 and C50–H1141. The larger the angle between the chemical bond and the axis of the applied shear, the stronger the shearing action, so the chemical bonds are more easily broken thereunder. When the angle between the chemical bond and the applied shear is less than 30° while breaking, $|\Delta R| > 0.100$. The smaller the angle, the stronger the tensile action, so the chemical bonds are easily broken under tensile action.

### 4.2. Effects of Bond Strength and Bond Angle on Breaking of Chemical Bonds under Shear

When the force constant $\frac{\Delta R}{\theta}$ was used to measure the strength, different types of bonds can be compared. The model was optimized, and the frequency was calculated at the B3LYP level of density functional theory, $^{33-35}$ using the Def2-SVP(P) basis set $^{38}$ with the DFT-D3 dispersion correction $^{39}$ in Gaussian software. After verifying that the optimized structure is at the minimum point by checking the calculated results, the file of calculated wave functions is imported into the compliance software $^{32,40}$ to output the relaxed force constant of chemical bonds (bond angle). The results are listed in Table 5.

It can be observed from Table 5 that the overall trend of the bond strength of broken chemical bonds of this coal macromolecules is as follows: C–C single bonds, hydroxyl O–H on the benzene ring (affected by ketonic bonds), bridge-bound C–H or C–H on the side chain, large $\pi$-bonds, hydroxyl O–H on the benzene ring are the weakest bonds for breaking under shearing action.

### Table 4. ΔR Data Statistical Table of No. 1 Molecule in Given Coal

| bonds | $\Delta R$ (Å°) | bonds | $\Delta R$ (Å°) | bonds | $\Delta R$ (Å°) | bonds | $\Delta R$ (Å°) |
|-------|----------------|-------|----------------|-------|----------------|-------|----------------|
| O112–H198 | 0.058 | C39–C99 | 0.167 | C94–C95 | 0.451 | C41–C42 | −1.792 |
| C50–H141 | 0.092 | C97–C98 | 0.254 | C43–C44 | 0.855 | C96–C97 | −54.897 |
| O93–H183 | 0.100 | C80–C81 | 0.340 | C72–C73 | −0.829 |      |                |

### Table 5. Statistics of Relaxed Force Constant about Bonds Broken by Shear Action in Given Coal

| bonds | relaxed force constant | bonds | relaxed force constant | bonds | relaxed force constant | bonds | relaxed force constant |
|-------|------------------------|-------|------------------------|-------|------------------------|-------|------------------------|
| C41–C42 | 2.611 | C44–C45 | 4.505 | C17–C18 | 5.917 |
| C42–C39 | 3.534 | C37–C39 | 4.587 | C18–C23 | 5.952 |
| C36–C42 | 3.610 | C65–H155 | 4.785 | C96–C97 | 6.135 |
| C39–C40 | 3.846 | C81–H170 | 4.878 | C61–C62 | 6.173 |
| C82–C87 | 4.016 | C80–H169 | 4.902 | C19–N24 | 6.250 |
| C80–C81 | 4.098 | C95–C103 | 4.926 | C94–C99 | 6.289 |
| C43–C44 | 4.115 | C87–H175 | 5.000 | C94–C95 | 6.803 |
| C81–C86 | 4.132 | C25–C28 | 5.155 | C67–C68 | 6.944 |
| C64–C65 | 4.237 | C76–H166 | 5.208 | C29–C30 | 7.519 |
| C59–C59 | 4.292 | C50–H141 | 5.263 | O1–H115 | 7.576 |
| O112–H198 | 4.292 | C55–H144 | 5.263 | C26–C27 | 7.634 |
| C72–C73 | 4.310 | C73–H159 | 5.376 | C41–C47 | 7.874 |
| O93–H183 | 4.367 | C58–H153 | 5.405 |      |                |
| C26–C34 | 4.386 | C97–C98 | 5.747 |      |                |

Figure 5. Schematic of the shear action mechanism. Adapted with permission from ref 31. Copyright 2021 Elsevier B.V.
4.3. Breaking Mechanisms of Chemical Bonds on Ring Structures (Including Large π-Bonds) under Shear. Ring structures in the coal macromolecules can generate a ring-opening reaction under tensile action (applied by the shear action) and can be easily attacked by surrounding molecules, leading to ring-opening reactions under tensile action. The average local ionization energy (ALIE) can be used to investigate reaction activity and sites of molecules. By combining data with Visual Molecular Dynamics (VMD), the ALIE of the coal macromolecules was obtained using Multifınów software for reduced density gradient (RDG) analysis.

Figure 6 shows the nine areas with the minimum ALIE in the coal macromolecules, namely, ① C2, C5, C11, and C14; ② C17, C20, N24, and C27; ③ C30, C33, C35, and C38; ④ C40, C41, C43, C44, C45, C46, and C47; ⑤ C51, C52, C53, and C54; ⑥ C59, C60, C61, C62, C63, and C64; ⑦ C68, C70, and C72; ⑧ C85, C86, C88, C89, C90, and C91; and ⑨ C95 (only white point), C96 (only white point), and C98 (only white point). They appear near the conjugate ring, on which some atoms and electrons are weakly bound. When other molecules act, the ring-opening reaction readily occurs to generate free radicals. Based
shear as applied by surrounding molecules, resulting in shear breaking.

(2) The shear action can not only break chemical bonds but also generate new chemical bonds. The shear stress does not destroy all of the chemical bonds but only the chemical bonds with low bond energy in coal.

(3) As the angle between the bond and the action direction exceeds 90°, the early shear action on bonds shows the effect of both shear and tension. The chemical bonds connected to atoms nearest to the area with the minimum ALIE are easily broken due to the shear action.

(4) Due to the effects of the shearing action, small molecules (such as H* and "CO) are separated from the Given macromolecules and the coal molecular chain is thus shortened, however, these free radicals combine with each other to produce many small gas molecules, such as H2 and CO.

5. CONCLUSIONS

By applying the shear action on the polymer model of medium-rank coal with a cross-linked structure by LAMMPS software, the response of the coal macromolecular structure in the shear process was obtained. The mechanisms were analyzed through quantum chemistry software. The following conclusions can be drawn:

(1) The bridge bonds of the ring structure and large π-bonds are readily subjected to shear and tensile actions, finally experiencing tensile breaking. Atoms (atomic clusters) in the outermost of coal macromolecules tend to undergo

Figure 6. ALIE distribution on the surface of Given coal macromolecules (blue represents the minimum area).
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