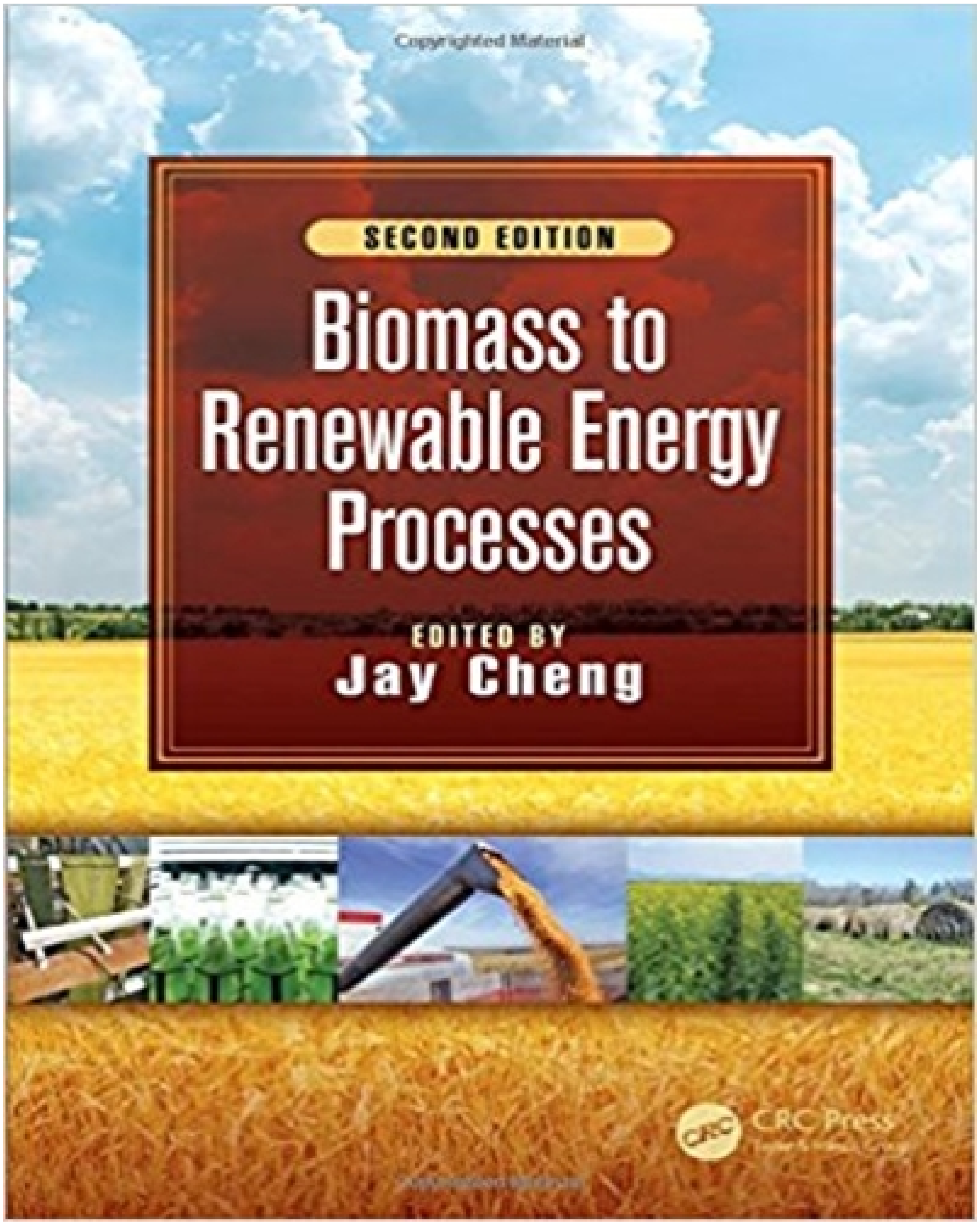
Solutions for Biomass to Renewable Energy Processes 2nd Edition by Cheng

CLICK HERE TO ACCESS COMPLETE Solutions

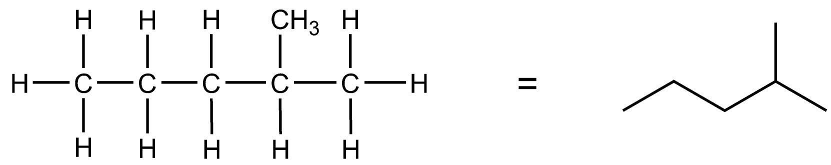


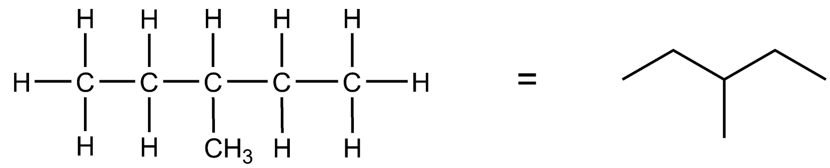
Solutions

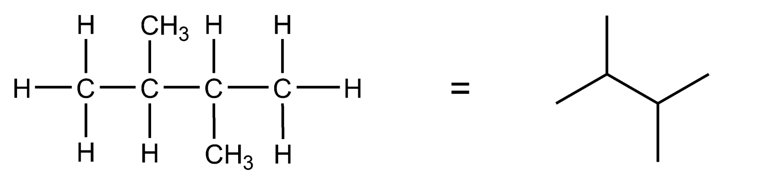
Problem Solutions for Chapter 2: Biomass Chemistry

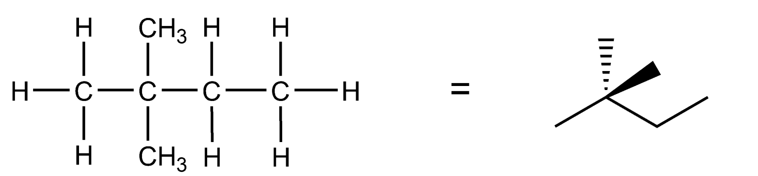
Problem 1. Draw all possible structural isomers for hexane, an alkane with an empirical formula of C_6H_{14}.

<u>SOLUTION:</u>









Problem 2. Explain *cis-trans* isomerism. What are the requirements for such isomerism to occur?

SOLUTION:

Cis-trans isomerism (or geometric isomerism) is a form of stereoisomerism that describes the orientation of functional groups in a molecule. This type of isomerism is typically seen when a double bond is present in a molecule. However, they can also be observed in ring structures. A key requirement is the presence of two identical functional groups attached to neighboring atoms that are linked via a double bond. In *cis* isomers, these identical functional groups are on the same side of the plane of the double bond, and in *trans* isomers, they are on opposite sides of the plane of the double bond.

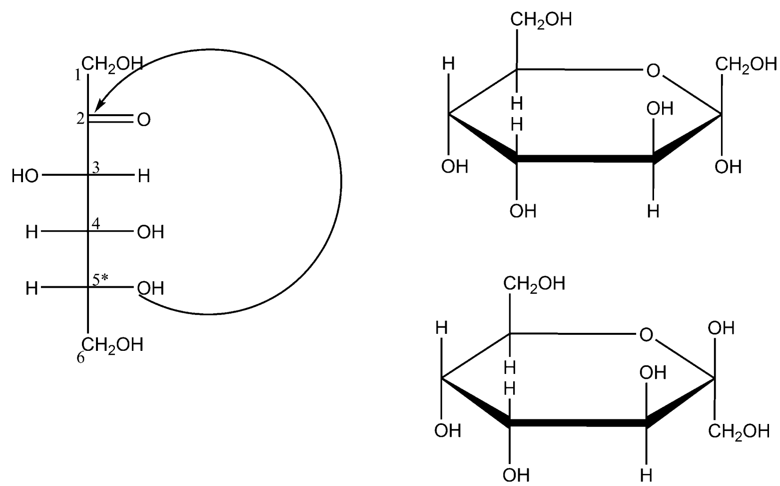
Problem 3. Differentiate between aliphatic and aromatic organic compounds and explain the phenomena of resonance structures in aromatic compounds.

SOLUTION:

Aliphatic compounds are those in which all electron pairs in the compound belong to either a single atom and/or shared between atoms. A simple example of an aliphatic compound is ethane. In contrast, aromatic compounds are those in which some electron pairs cannot be assigned to a specific atom or pair of atoms. Such compounds contain a conjugated ring of alternating single and double bonds. An example of an aromatic compound is benzene. Benzene contains a conjugated ring of alternating single and double bonds. Since, it is impossible to specify the exact location of the double bonds in the benzene ring, two possible structures are possible and they are collectively termed as resonance structures of benzene.

Problem 4. Draw the α and β anomers of the pyranose ring formed from the open-chain structure of fructose shown in Figure 2.12.

SOLUTION:



Problem 5. What are the differences between amylose and amylopectin?

SOLUTION:

- Amylose has a lower molecular weight (MW) than amylopectin (10^5-10^6 g/mol vs. 10^7-10^9 g/mol)
- In amylose, D-glucopyranose units are linked via α-1,4 glycosidic bonds and in amylopectin, D-glucopyranose units linked via α-1,4 glycosidic bonds with non-random α-1,6 linked branching. The branching causes amylopectin to be relatively non-crystalline in comparison to amylose.
- The helical structure of amylose results in the formation of clathrate complexes. Amylopectin does not tend to form clathrate complexes.

Problem 6. Explain why cellulose exhibits more crystallinity than amylose or amylopectin.

SOLUTION:

Unlike amylose or amylopectin, the glycoside linkage in cellulose is β-1,4. The angle of the β-1,4 glycosidic bond results in linear cellulose chains that enable strong intra- and inter-molecular hydrogen bonding. Two types of intra-molecular hydrogen bonding occur within the same chain. The first type is between the endocyclic oxygen (oxygen atom in the ring) and the hydrogen atom in the OH group of the C3 carbon (of a neighboring glucose). The second type is between the oxygen atom in the OH group of the C6 carbon and the hydrogen atom in the OH group of the C2 carbon (of a neighboring glucose). Between cellulose chains, there is a single intermolecular hydrogen bond between the hydrogen atom in the OH group of the C6 carbon and the oxygen atom in the OH group of the C3 carbon atom. These hydrogen bonds enable the formation of microfibrils from individual cellulose chains resulting in a high degree of crystallinity.

Problem 7. What are the differences between hemicellulose and cellulose?

SOLUTION:

- Cellulose is a homopolymer of glucose, whereas hemicelluloses are branched heteropolymers with monomer units that include pentoses (arabinose and xylose), hexoses (glucose, galactose, mannose, rhamnose and fucose) and uronic acids (galacturonic, glucuronic and methylglucuronic).
- Hemicelluloses have a lower degree of polymerization in comparison to cellulose

- Hemicelluloses have a random amorphous structure whereas cellulose has a rigid crystalline structure.
- Hemicelluloses have low thermal stability compared to cellulose.

Problem 8. Distinguish between the major and minor hemicelluloses of hardwoods, grasses and softwoods.

SOLUTION:

- In hardwoods and grasses, the major hemicelluloses are xylans and the minor hemicelluloses are glucomannans. In softwoods, the major hemicelluloses are glucomannans and the minor hemicelluloses are xylans.
- Hardwood xylans contain glucuronic acid residues and acetyl groups, grass xylans contain arabinose residues and acetyl groups and softwood xylans contain arabinose and glucuronic acid residues.
- Softwood glucomannans contain galactose residues but hardwood and grass glucomannans rarely contain any substituent groups.

Problem 9. Define resonance in the context of aromatic compounds and explain the role of resonance structures in the biosynthesis of lignin.

SOLUTION:

See solution to problem 3 for first part of the question. The polymeric structure of lignin is formed by enzyme-catalyzed dehydrogenation of individual monolignols. A free radical formed on the phenolic oxygen can be transferred to other atoms of the monolignol to form resonance-stabilized structures. The presence of the free radical at different positions enables a number of different types of carbon-carbon and ether bonds responsible for the formation of dimers, trimers and tetramers that make-up the eventual complex structure of lignin.

Problem 10. The cloud point is an indicator of biodiesel performance at low temperatures. It is defined as the temperature at which crystals start to form in the fuel. As the temperature is further lowered, the fuel starts to solidify. Explain why biodiesel produced using palm oil has a much higher cloud point than biodiesel produced from canola or soybean.

SOLUTION:

Based on data from Table 2.2 in the book, the dominant fatty acid in palm oil is palmitic acid, which is a saturated fatty acid, and the dominant fatty acids in canola and soybean are oleic acid and linoleic acid, respectively, which are both unsaturated fatty acids. The presence of double bonds in oleic and linoleic acids enable *cis-trans* isomerism. The presence of *cis* isomers can result in triglycerides that are packed in a less compact manner and consequently the biodiesel formed from these triglycerides will solidify at a much lower temperature.