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微波热解木质生物质的研究进展

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摘要: 随着化石资源的日益枯竭及环境污染问题的日益严峻, 开发与利用环境友好的可再生资源受到广泛关注。木质生物质微波热解具有反应速率快、易于控制、安全无污染等优点, 但是存在产物分布不均和经济价值不高等问题, 严重制约了生物质能的全面与高效利用。系统地介绍了木质纤维素组分的结构, 详细阐述了木质纤维素各组分的热解机制, 并比较了微波热解与传统热解的差异, 探讨了微波热解的影响因素以及微波催化热解木质纤维素的产物分布。此外, 介绍不同种类催化剂(碳基材料、分子筛、金属氧化物等)在促进生物质微波热解中的作用, 可以高效转化木质纤维素, 优化微波热解产物的种类分布, 并促进选择性生产特定高值化学品, 以实现木质纤维素的资源化和高值化利用。最后, 对木质纤维素热解未来研究方向和技术发展进行了展望。

关键词: 木质纤维素生物质; 微波热解; 化学品; 催化

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Recent advances in the microwave pyrolysis of lignocellulosic biomass

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Abstract: With the increasing depletion of fossil resources and the growing serious environmental pollution, the development and utilization of environmentally friendly renewable resources have drawn widespread attention. Microwave pyrolysis of lignocellulosic biomass offers advantages such as fast reaction rates, easy control, and pollution-free operation. However, issues such as uneven product distribution and low economic value severe restrict the comprehensive and efficient utilization of biomass energy. This review systematically introduces the structure of lignocellulosic components, elaborates on the pyrolysis mechanisms of each component, compares the differences between microwave pyrolysis and traditional pyrolysis, discusses the influencing factors of microwave pyrolysis, and examines the product distribution of microwave-catalyzed pyrolysis of lignocellulosic biomass. Furthermore, various catalysts (carbon-based materials, molecular sieves, metal oxides, etc.) that promote microwave pyrolysis of biomass are introduced. These catalysts efficiently convert lignocellulosic biomass, optimize

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the distribution of microwave pyrolysis products, and facilitate the selective production of specific high-value chemicals, thereby promoting the resource utilization and value-added utilization of lignocellulosic biomass. Finally, the review presents prospects for future research directions and technological developments in lignocellulosic pyrolysis.

Keywords: Lignocellulosic biomass; Microwave pyrolysis; Chemicals; Catalysis

0 引言

全球人口的增加和经济发展对能源需求日益增长。尽管能源种类不断涌现,但液态烃燃料(通常为汽油和柴油)仍占全球总能源消耗的约 20.0%,并主导着现有能源基础设施^[1]。与此同时,工业和日常生活对石化产品的需求仍处于较高水平。由于化石资源日益枯竭和环境问题,用于石化产品和运输燃料的可再生和可持续替代品正在被广泛开发^[2]。其中,木质纤维素类生物质由于其来源广泛、可再生、低成本的特性,已得到大家的广泛关注^[3-5]。

木质纤维素生物质是具有巨大前景的可再生能源资源^[6],可以从农业和森林残留物、多年生木材、城市 and 工业废物等原材料中获得^[7]。生物质热解能够回收生物质原料的化学值和热值,是一种可行的热化学转化途径^[8]。这种转化方法可以产生高达 70.0%~95.0%的生物油产量^[9-10]。生物质热解的温度范围一般为 300~1 000 °C^[11]。常规快速热解产生的生物油馏分分布广泛^[12],催化生物质快速热解可提高生物油馏分的品质^[13]。热解生物油的主要成分是酸、醛、酮、呋喃、酚和烷基化(聚)酚,以及相对少量的酚、丁香酚、甲酚和二甲苯酚^[14]。这些热解产物可以进一步通过加氢脱氧反应转化为高品质的液体燃料或者平台化合物^[9, 15-16]。此外,生物质热解产生的生物质炭也具有多种用途^[17-20]。与传统热解方法比较,微波热解技术具有许多优点,包括快速均匀地加热大块原料、生产高质量和稳定性的生物油^[21]以及快速启动和关闭的瞬时响应^[22]。一些研究人员认为微波热解转化途径可用于处理大量生物质原料^[23-24]。比较研究表明,由于微波辐射的快速加热效应,与传统电炉热解相比,微波热解产生更多的生物油^[25-26]。

本综述将重点论述木质纤维素生物质微波热解的最新研究进展,对木质纤维素的组分、热解机制进行系统介绍,并重要讨论微波辅助热解(Microwave Assisted Pyrolysis, MAP)中的热解条件、催

化剂种类对产物的影响。

1 木质纤维素的结构

木质纤维素生物质主要由纤维素、半纤维素和木质素组成,如图 1 所示。纤维素是由 $\beta(1-4)$ 糖苷键连接葡萄糖分子形成的巨大直链分子,是生物质中最丰富的成分^[27],占 40%~60%。直链包含 20~300 个葡萄糖单元。葡萄糖单元上的 C2、C3 和 C6 含有大量羟基,羟基中的氧原子和氢原子之间可形成大量的分子内和分子间氢键。大量氢键的存在诱导纤维素结晶区的形成。纤维素链的不同排列方式可以形成无定型区和结晶区,并且结晶区具有不同的晶型。通常情况下,常规溶剂只能进入无定型区而很难接触结晶区,从而导致纤维素很难在常规溶剂中溶解^[28]。

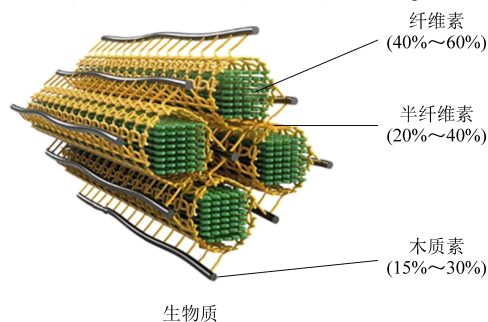


图 1 生物质的木质纤维素成分^[29]

Fig. 1 Lignocellulose composition of biomass^[29]

半纤维素是木质纤维素生物质的另一种主要结构成分,占 20%~30%。半纤维素主要由戊糖、己糖(葡萄糖、半乳糖和甘露糖)和糖醛酸(D-半乳糖醛酸、4-O-甲基葡萄糖醛酸和其他 D-葡萄糖醛酸化合物)通过糖苷键链接而成。半纤维素的主链可由一种或几种糖原(木糖、甘露糖等)组成,如果是由两种及以上的糖原组成,这些糖基之间的连接方式也各不相同。此外,木质素主链还链接不同聚合单糖的短侧链,构象各异的支链使半纤维素的结构变得更加复杂,而且对半纤维素的性质具有重大影响。与纤维素相比,半纤维素是一种无定形有机聚合物,其结构更容易受到热处理和化学处理的影响。

木质素是木质纤维素生物质中唯一的芳香族聚合物成分,占 15.0%~25.0%,其在植物木质纤维素生物质中的比例取决于不同种类的生物质原料。木质素是由对羟基苯丙烷、愈创木基和紫丁香基三种基本结构单元交联而成的三维网状芳香聚合物^[30]。木质素主要是通过醚键(α -O-4、 β -O-4)和碳碳键(β -5 和 β - β 键)链接不同结构单元而成,其中 β -O-4 键是木质素中最主要的链接方式^[31]。木质素主要位于纤维素和半纤维素之间,并赋予植物机械强度,从而使其具有抗压能力并可抵抗病原感染。木质素是木质纤维素中最不易热解的成分,并且生物油中的酚类物质主要来源于木质素^[32]。

2 木质纤维素催化热解

木质纤维素生物质的热解是一种热化学分解过程,一般反应温度在 500~700 °C 范围内进行。生物质原料热解产物包含生物合成气、生物油和生物炭^[33]。此前的研究表明,生物质热解过程中同时发生了几种化学反应,包括脱水、解聚、异构化、脱羧、芳构化和碳化^[34]。由于生物质结构的特点,热解是一个在空间和时间尺度上的多阶段分解和反应的过程。基于木质纤维素生物质的组分,热解过程包括三个主要步骤,包括自由水分蒸发,然后进行初次裂解和二次反应^[35]。在 200~400 °C 下,纤维素发生初级分解形成固体炭。在 250~350 °C 时,半纤维素分解形成木聚糖,其特征是产生左旋葡聚糖和呋喃作为主要热解产物^[36]。温度的进一步升高导致左旋葡聚糖和呋喃转化为轻质含氧化合物和呋喃。随着温度的升高,固体基质中也会发生二次反应。木质素在 325~400 °C 时降解,热解过程中的较低温度导致单木质素的形成,而较高温度促进反应进一步形成酚和含氧较少的化合物。

2.1 纤维素热解机制

纤维素热解的初始产物主要是脱水糖和呋喃化合物。在生成脱水糖之后,通过脱水、键断裂以及气相中的键重排,生成呋喃类物质,如呋喃、甲基呋喃,糠醛和水,如图 2 所示是纤维素热解的主要反应。

2.2 半纤维素热解机制

半纤维素的木聚糖发生热解反应后得到一种重要的挥发分产物,即糠醛,而且大部分关于木聚糖热解反应的研究中都能发现糠醛的存在。糠醛

可以通过木聚糖的支链上的糖基单元 4-甲基-D-葡萄糖醛酸通过一系列的反应得到,也可以通过木聚糖的主链上的糖基单元即 D-木糖单体通过一系列的脱水反应而得到。支链上的 4-O-甲基-D-葡萄糖醛酸单元的反应在温度较低时,木聚糖的热解反应主要是发生在支链上,4-O-甲基-D-葡萄糖醛酸发生如图 3 所示的分解过程。首先是杂环上的甲氧基脱离,这一部分形成了甲醇,然后发生脱酰基反应,剩下的吡喃糖单元连续发生两个脱水反应,由六元环变成五元环,生成一个糠醛分子和两个水分子。

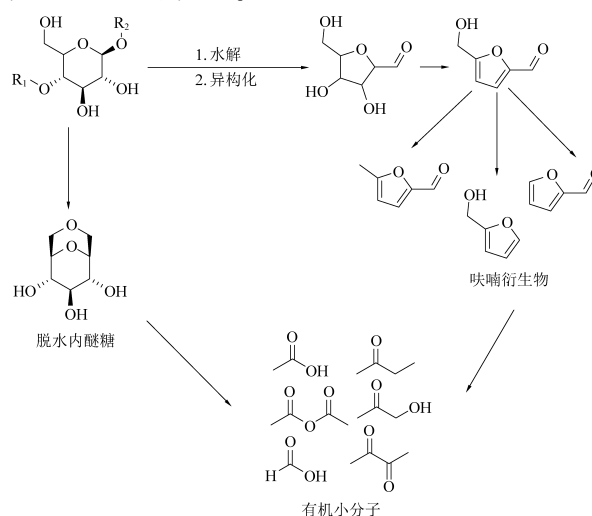


图 2 纤维素在微波辅助热解过程中发生的主要反应^[37]

Fig. 2 Main reactions occurring during cellulose microwave-assisted pyrolysis^[37]

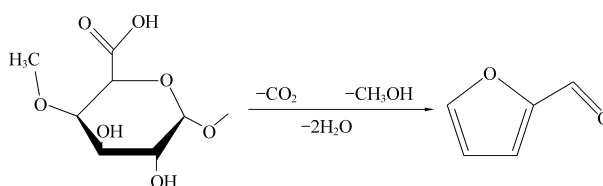


图 3 半纤维素在微波辅助热解过程中发生的主要反应

Fig. 3 Main reactions of hemicellulose during microwave assisted pyrolysis

主链上的 D-木糖单体随着反应温度的升高,木聚糖的主体结构即主链发生解聚反应,这时主链慢慢分解为糖基单元。糖基单元 D-木糖单体再发生进一步分解,通过一系列的反应得到各种小分子化合物,其中包括大聚糖热解的典型产物糠醛。图 4 显示主链上 D-木糖单元脱水生成糠醛的反应途径。

2.3 木质素热解机制

木质素热解中可能的热解机制如图 5 所示。在低于 200 °C 时,木质素首先发生软化反应,也称为玻

璃化转变,其中木质素转化为几种液体中间体^[38]。第二阶段发生在 200~350 °C,涉及中间体的解聚,并转化为芳香醇,称为单二醇,包括针叶树醇、辛那基醇和对肉桂醇。然后,通过切断 C=O 键和 C=C 键,芳香醇转化为甲氧基苯酚,即 2-甲氧基-4-乙烯基苯酚^[39]。随着温度持续升高至 350 °C 以上并达到 500 °C,甲氧基酚通过脱烷基化和脱甲氧基化过程,可得到烷基酚和苯酚等化学品^[40]。最后,高于 500 °C,甲氧基酚将进行二次降解,生成脂肪族和甲醇^[41]。

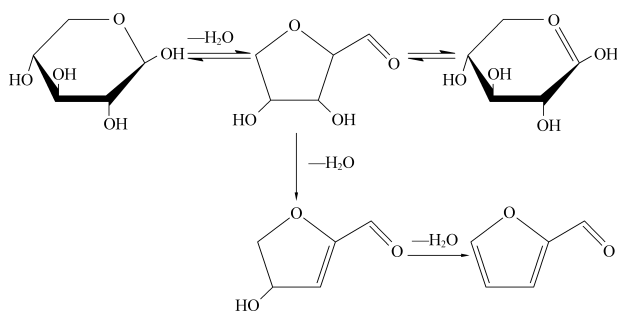


图4 主链上 D-木糖单元脱水生成糠醛的反应途径
Fig. 4 Reaction path of dehydration of d-xylose unit on main chain to furfural

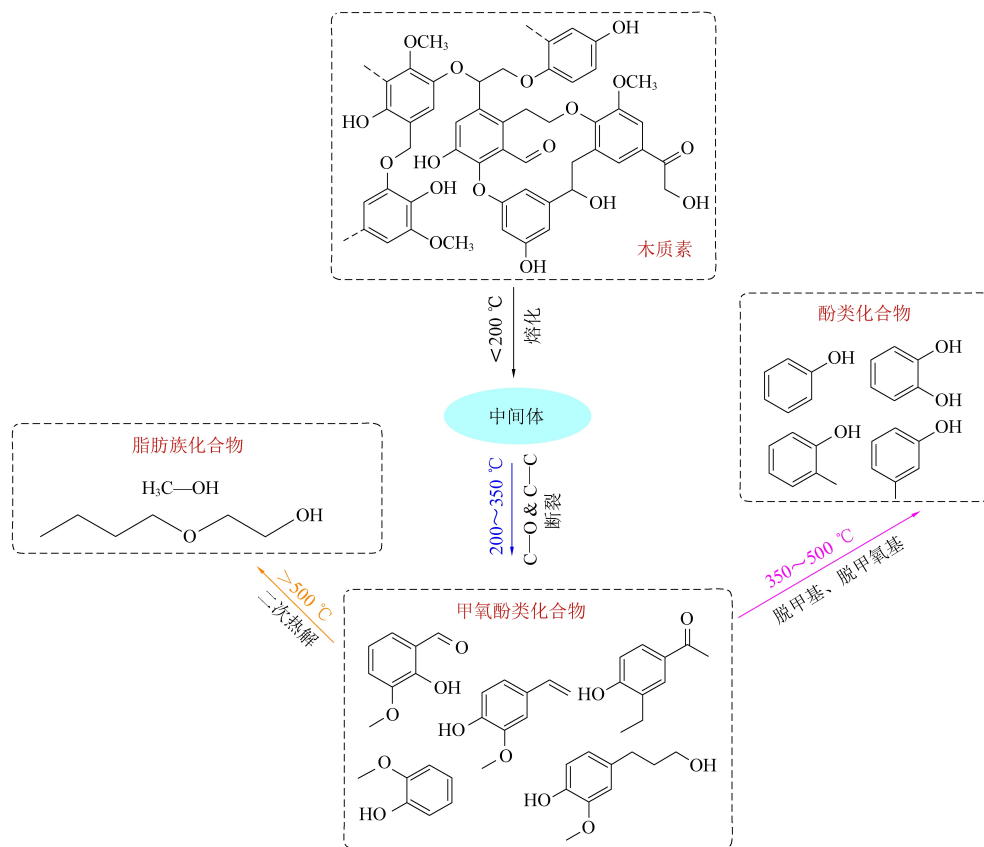


图5 木质素热解可能的反应机理方案^[35]

Fig. 5 Possible reaction mechanism and scheme of lignin pyrolysis^[35]

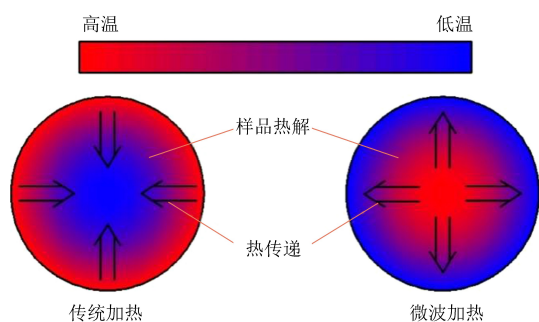
3 生物质催化微波热解

3.1 微波热解与传统热解对比

传统热解技术和微波热解技术在传热模式上有所不同。在传统加热中,通过对流和热传导,热量从材料表面转移到中心,在微波热解中,材料中的热量是通过物料中带电粒子与穿透力极强的电磁波发生相互作用,粒子之间经过剧烈碰撞、摩擦和挤压进行产热,电磁能直接转化为内能,由于电磁波与反应物的直接相互作用,均匀加热,并且在热解的时候不需要原料研磨,还会产生具有前景

的生物油^[42]。

传统加热存在一些缺点,例如热能量损失、过程的不可控性、副反应多、表面非选择性加热以及更长的停留时间等,并且较大的生物质颗粒会增加温度梯度,从而影响局部加热速率,而较小的生物质颗粒会增加生物油的产量^[44]。然而在微波热解中,生物质颗粒大小影响并不明显,因为微波热解是从内部加热,所以具有加热速率快、均匀性好及预处理成本低等特点。生物质传统热解与微波热解的比较如图6所示^[43]。

图6 生物质传统热解与微波热解比较^[43]Fig. 6 Comparison between traditional pyrolysis and microwave pyrolysis of biomass^[43]

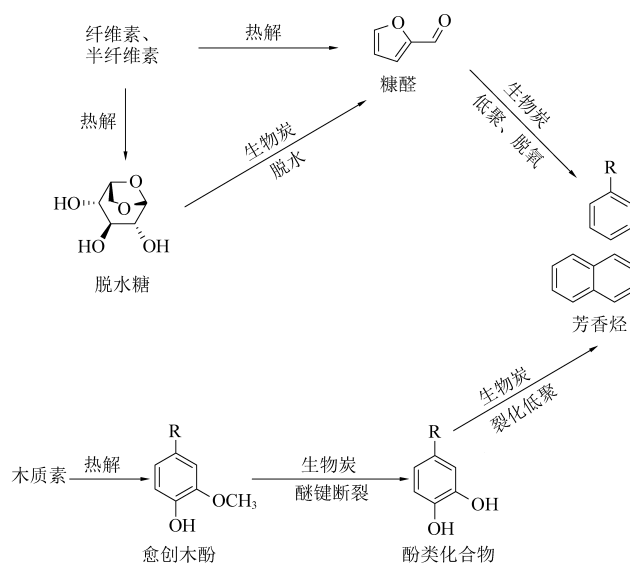
3.2 木质纤维素微波催化热解

在木质纤维素生物质微波热解过程中,微波吸收剂被广泛用于帮助加热介电性较差的生物质原料。由于生物质原料的复杂性,在热解时,产物产率也随着原料的变化而变化,因此在微波热解中引入催化剂来调控对生物油中所需化合物的选择性,改变生物炭的结构和化学性质,并调整不凝气体的组成。微波吸收剂和催化剂是微波热解中的两种重要添加剂,分别用于提高微波热解过程中生物质加热的性能和热解产物的选择性。如果单一固体添加剂既可以用作催化剂又可以用作微波吸收剂,那么这种催化剂较为理想。目前作为生物质微波热解的催化剂主要包括活性炭、金属氧化物、分子筛等。

3.2.1 碳基材料微波催化热解

活性炭在生物质微波催化热解过程中表现出对苯酚较好的选择性。大量研究表明,通过商用活性炭催化热解生物质,可以在生物油中获得相对较高的酚含量^[45-46]。稳定实验结果表明,活性炭催化剂可以保持良好的性能,可显示出微孔结构^[47],并被检测出具有高表面积^[48]和高碳含量(这表明吸收微波辐射并将其转化为热的能力很高)。这些结果表明,活性炭可以用作微波吸收剂,通过加热目标材料以实现高温裂解,同时为发生裂解反应提供许多反应位点,让目标材料能够生成更多所需要的裂解产物。当活性炭用于杉树的微波热解时,使用活性炭产生的生物油中的苯酚含量(质量分数 34.0%~39.0%)远高于不使用活性炭的生物油(<1.0%)^[49]。随着温度从316 °C升高到 400 °C,生物油产率从 12.5%增加到 31.0%,但在 484 °C时降低到 26.4%。484 °C时产生的合成气更多(57.5%),生物炭更少(18.9%)。将活性炭与生物质的比率从 1.3 提高到 4.0,可改

善液体(从 30.2%提高到 38.3%)和气体(从34.8%提高到 50.4%)的产量。在 316 °C、活性炭与生物质的比例为 3 : 1、反应时间为 8 min 的条件下,达到酚类化合物最大产率(质量分数 66.9%)。另一项研究发现^[50],在相同温度(400 °C)下,活性炭与杉树的比率分别为 0.094 和 1.150,生物油产量最高为 25.5%,最低为 12.5%。研究还显示了活性炭与杉树的比率与苯酚产量之间呈正相关关系^[51-52]。通过活性炭催化剂的快速热解工艺将生物质转化为富含烃类的生物油的主要机理如图 7 所示^[53]。对于生物质在活性炭催化剂上的快速热解过程,芳烃的生成主要由两部分组成:(1)葡萄糖、无水糖和呋喃可以从纤维素和半纤维素的降解中产生。葡萄糖在热解过程中可以通过活性炭的酸位点脱水成无水糖,然后,产生的无水糖可以通过脱水反应转化为呋喃。同时,呋喃最终可以通过脱羰基化、脱羧和低聚反应转化为芳烃;(2)生物质原料中的木质素可以降解为愈创木酚,首先通过裂解甲氧基团转化为酚类,然后通过裂解酚羟基将所得酚进一步转化为芳烃^[54-55]。

图7 碳基催化剂微波快速热解生产芳烃的生物油升级机理^[53]Fig. 7 Upgrading mechanism of bio oil for aromatics production by microwave rapid pyrolysis on carbon based catalysts^[53]

3.2.2 金属氧化物微波催化热解

一些简单的金属氧化物(如 CaO、NiO、CuO、MgO 等)由于其在催化热解过程中,特别是微波辅助催化热解过程,能够抑制重焦油的形成而引起广泛的关注^[56]。研究发现,金属氧化物作为生物质微波热解中的催化剂,可以在相对较低的微波功率下提高热解反应温度,提高生物油和生物炭

的质量,并影响生物炭、生物油和沼气三种主要产品的产品分布。由于其高介电常数,金属氧化物还可以通过充当微波吸收剂来提高工艺能量转化效率^[57]。

MORGAN 等^[58]研究了一些金属氧化物催化剂(NiO、CaO、CuO 和 MgO),因为它们对气体和液体产量有积极影响,所以这些催化剂会导致炭产率下降。CuO 或 MgO 可以增加 H₂ 含量,而 CaO 和 MgO 对增加总气体产量产生积极影响。此外,NiO 或 CuO 可用于增加液体产量。结果表明,在 N₂ 气氛下碱土金属氧化物催化剂的性能优于在 CO₂ 气氛下,这可能是由于 CO₂ 和 N₂ 的辐射吸收不同。MUSHTAQ 等^[59]报道 Fe₃O₄ 可提高合成气产率,对于芳香族和脂肪族烃的裂解行为,不同氧

化物的催化顺序为 Fe₃O₄ > Al₂O₃ > CaO > SiO₂。WANG 等^[60]研究了一系列复合金属氧化物,包括 ZrO₂/γ-Al₂O₃、CeO₂/γ-Al₂O₃ 和 ZrO₂-CeO₂/γ-Al₂O₃ 分别对竹子微波热解行为的影响,实验结果表明,与无催化剂试验相比,金属氧化物的使用促进了酮和单芳烃的形成。在金属氧化物中,ZrO₂-CeO₂/γ-Al₂O₃ 表现出最显著的酮化和羟醛缩合活性,产生最高浓度的线性酮和环状酮。此外,非酸性含氧化合物如糠醛、乙醛、丁二醛、2,3-二氢苯并呋喃和乙酸甲酯可通过金属氧化物有效转化为烃前体,而 ZrO₂-CeO₂/γ-Al₂O₃ 与竹屑混合热解可提高苯、甲苯和烷基苯的浓度。表 1 列出了不同金属氧化物微波热解生物质的产物分布情况。

表 1 不同类型的金属氧化物催化剂对生物质微波热解产物分布的影响

Table 1 Effects of different types of metal oxide catalysts on the distribution of biomass microwave pyrolysis products

生物质	条件		炭/%	油/%	气/%	产物	文献
	催化剂	温度/℃					
地沟油	CaO	550	4.0	66.0	30.0	芳香烃 61.7%, MAHs 23.7%, PAHs 20.3%	[61]
食品废弃物	Fe ₃ O ₄	1 000	17.9	17.1	65.0	碳氢化合物 66%, 含氧化合物 14.7%	[62]
食品废弃物	Fe ₂ O ₃	1 000	19.5	18.2	62.3	碳氢化合物 67.5%, 含氧化合物 18.2%	[62]
木质素-低密度聚乙烯	MgO	550	42.1	36.4	21.5	碳氢化合物 49.1%, 酚 14.3%	[63]
紫茎泽兰	ZnO	500	26.1	28.8	45.1	烷烃 28.2%, 酚 21.3%	[64]

3.2.3 分子筛微波催化热解

自然界中存在一种天然硅铝酸盐,具有筛分分子、吸附、离子交换和催化作用。这种天然物质称为沸石,人工合成的沸石也称为分子筛。分子筛是一种铝硅酸盐,按照孔道半径划分,小于 2 nm 为微孔分子筛,在 2~50 nm 之间为介孔分子筛,大于 50 nm 为大孔分子筛,具有独特的孔结构、较高的催化活性和热稳定性及耐酸性等特点,通常用作微波吸收剂和催化剂。由于其酸性和形状选择性^[65],分子筛也是生物质热解和生物油升级中最常用的催化剂之一。以下介绍了几种类型的人工合成沸石用于生物质的微波热解,包括 ZSM-5、SBA-15 和 HZSM-5。

ZSM-5 应用于杉木颗粒的微波热解中,以增加生物油中芳烃和酚的含量^[66]。根据热解条件,发现生物油中 50%~82% 的化合物为酚类、愈创木酚和芳香烃。通过在核壳分级沸石催化剂上进行生物质热解,可以提高生物油的质量。WEI 等^[67]报告称,与 SiO₂/Al₂O₃ 比为 25 的传统 ZSM-5(25)相比,ZSM-5(25)@SBA-15 不仅使生物油产量增加至 40.0% 以上,还在椰子壳微波辅助热解过

程中,碳氢化合物的产量增加了约一倍。

ZHAO 等^[68]研究了在微波辅助下 HZSM-5 (图 8)对竹子和聚丙烯(PP)的催化共热解制备生物油的影响,研究了热解温度、原料/催化剂比和竹子/PP 比对共热解生物油产品收率和化学成分的影响。当催化温度、原料/催化剂比和竹子/PP 比为 250 ℃、1:2 和 2:1 时,产物中生物油占比达到最大值 61.6%,含氧化合物比例随催化剂

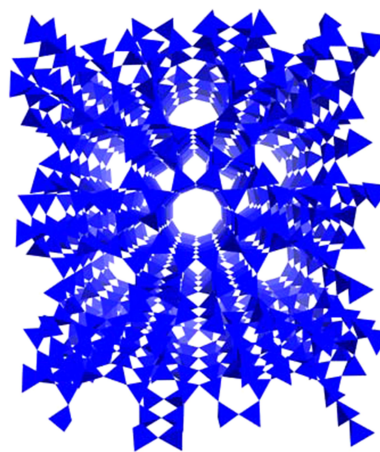


图 8 HZSM-5 结构

Fig. 8 Structure of HZSM-5

含量的增加而降低。PP 的加入改善了芳烃和环烷烃的比例。从航空燃料的角度来看,生物油质量得到了大幅升级。废塑料和固体生物质的共热解产生了协同效应,可以提高产品质量^[69]。塑料废物含有高氢碳比和相对较低的氧碳比,可以在共热解过程中改善生物质固有的高氧碳比和低氢碳比,从而提高产品的质量和均匀性,最大限度地减少纯塑料废物热解产生的焦炭沉积^[70]。共热解通过最大限度地减少对废物分离的要求,提供了一种有吸引力的途径^[71]。

3.3 微波热解的影响因素

许多研究小组正在致力于通过微波加热工艺将木质纤维素生物质和农业残留物转化为燃料、化学品和新型材料。影响产品产量及其质量的主要因素不仅包括催化剂,还有生物质原料、微波反应条件参数、反应器的设计等。通过调节这些影响因素,可以选择性调控木质纤维素生物质热解产物的种类及分布情况,从而更好地提高木质纤维素的利用价值和经济效益。

3.3.1 生物质原料类型

微波热解工艺的生物油产量也受母体生物质原料类型的影响。据报道,一方面,纤维素和半纤维素含量高的木质纤维素生物质可产生更多的生物油^[73-74];另一方面,灰分含量高的生物质产生的生物油较少,因为灰分成分不能转化为生物油。HASCAKIR 和 AKIN^[75-76]观察到,三种高灰分含量(60.5%至 70.9%)的油页岩的 MAP 获得了 0~0.24%的低生物油产率。

3.3.2 微波功率

通常,微波功率的增加会增加生物油产量,因为增加微波功率会导致功率密度的增加。在较高的功率密度下,热解速率和温度增加,导致生物油产量增加。MARTIN 等^[77]将微波功率从 300 W 增加到 400 W,使林业残渣的生物油产量从 45.0% 提高到 58.0%。图 9 显示不同功率对热生物油产率的影响。

3.3.3 保留时间

在大多数情况下,小型间歇式反应器已用于研究生物质原料的 MAP。在典型的间歇系统中,反应物的保持时间会影响生物油产率。据报道,在短停留期内,热解过程可能无法完成,导致生物油产量降低^[78-79]。

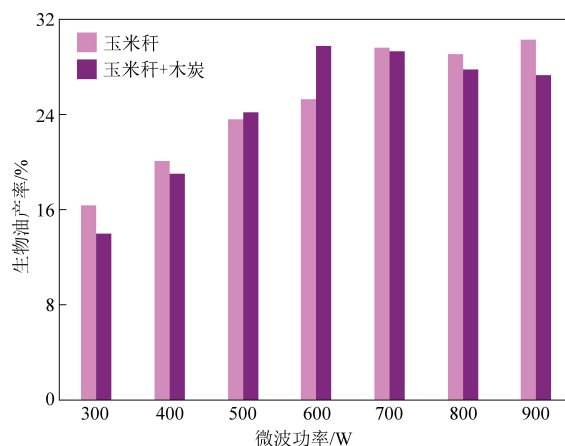


图 9 微波功率对微波热解生物油产率的影响^[72]

Fig. 9 Bio-oil yields through microwave-assisted pyrolysis at different microwave powers^[72]

4 总结与展望

本文详细介绍了木质纤维素生物质的结构以及木质纤维素各组分的热解机制,阐述了微波热解木质纤维素的影响因素、催化剂种类(碳材料、分子筛、金属氧化物等)对微波热解产物的影响。过往研究表明,生物质来源差异、微波热解生物质的产物复杂、微波设备影响因素多、产物回收困难、催化剂稳定性差是制约生物质热解技术应用的重要原因。目前的微波热解体系和常规催化剂难以很好地控制生产成本,催化剂的微波催化耦合作用机制不够清晰以及催化剂对产物选择性调控不够明确。因此,生物质微波热解的未来研究方向需要在微波设备的参数设计、微波热解对生物质裂解的动力学模型、催化剂对微波热解产物选择性、原位探究催化剂-微波热解的动力学分析以及热解过后对热解产物的有效分离提纯等方面进行,提高微波热解体系的整体经济性和环境可持续性,从而最终实现生物质微波热解技术的广泛应用。生物质微波热解技术将会为生物质高值化提供一条重要途径。

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