

木屑热解挥发物冷凝特性研究

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摘要: 在自行设计的生物质热解挥发物两级冷凝特性参数测试系统上,进行了木屑在 450、550、650℃下热解挥发物冷凝特性研究,其中,一级冷凝采用空气作为冷凝介质,二级冷凝采用水作为冷凝介质,计算了表面局部冷凝换热系数,以及冷凝液膜热阻和厚度。结果表明:一级冷凝换热系数随着温度的升高而减小,在热解温度为 450℃时达到最大值 671.02 W/(m²·K);二级换热系数随着温度的升高先增大后减小,在热解温度为 550℃时达到最大值 1.484 × 10⁵ W/(m²·K)。基于冷凝器内壁一维稳态冷凝换热特性,分析了冷凝液膜形成过程,存在 3 个阶段:液膜形成、液膜积累、液膜流动。在液膜形成和积累阶段,液膜厚度逐渐增大,热阻变大;液膜厚度达到一定程度后,冷凝液产生流动,在液膜流动初期,液膜厚度逐渐减小,热阻变小;在稳定流动期,热阻基本保持稳定。

关键词: 木屑; 热解; 冷凝特性; 换热系数; 液膜模型

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Condensation Characteristics of Volatile Matter from Sawdust Pyrolysis

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Abstract: Pyrolysis is a relatively simple, inexpensive, and robust thermochemical technology for transforming biomass into bio-oil, biochar and syngas. While the intention of slow pyrolysis is to produce mainly charcoal, fast pyrolysis is meant to convert biomass to a maximum quantity of liquids (bio-oil). Biochar can be used with existing infrastructure as a replacement for pulverized coal, bio-oil can be used as a fuel in existing industrial boilers. The pyrolysis of sawdust contains volatile bio-oil and non-condensing gas, so the condensation characteristics are different from those of other simple mixture. Based on the test system of biomass pyrolysis volatile matter condensation characteristic parameter, the experiment of condensation characteristics of pyrolysis volatile was carried out at 450℃, 550℃ and 650℃. The condensation characteristics of volatile matter produced at different pyrolysis temperatures were tested, and the heat transfer coefficient, the thermal resistance and thickness of condensation liquid film were calculated. Based on the one-dimensional heat transfer characteristics of liquid condensation, the condensate film formation process had three stages: formation, accumulation and flow of liquid film. The results showed that the first stage condensation heat transfer coefficient was decreased with the increase of temperature, biomass volatile surface heat transfer coefficient at 450℃ was the highest, which was 671.02 W/(m²·K); with the increase of temperature, the heat transfer coefficient of the second stage was increased first and then decreased, biomass volatile surface heat transfer coefficient at 550℃ was the highest, which was 1.484 × 10⁵ W/(m²·K). According to the experimental value and the hypothesis of condensate film, in the film formation and accumulation stage, the film thickness was gradually increased and the thermal resistance was decreased; early in the liquid film flow stage, with the decrease of the film thickness, the thermal resistance was decreased; in the steady flow stage, resistance was remained stable. The research result can provide reference for the on-line collection of bio-oil and the design of bio-oil condenser in continuous pyrolysis equipment.

Key words: sawdust; pyrolysis; condensation characteristics; heat transfer coefficient; liquid film model

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引言

我国生物质能源丰富^[1-2]。近几十年来热解被认为是一种很有前景的生物质利用技术^[3]。不同的热解条件能够产生不同比例的气、液、固三态产物:其中固体炭可以用作活性剂;含有 CO、CO₂、H₂、CH₄及饱和或不饱和烃类化合物等不可凝气体^[4]则可以用作工业或者民用燃气;液态生物油可进一步分离和提取,制成燃料油和化工原料,具有很高的利用价值。因此国内外研究人员针对热解装置和液体产物收集技术进行了相关研究,由于生物油主要由各类组分复杂的含氧不饱和和烃类衍生物组成^[5-10],目前分离生物油仍主要依靠常规冷凝手段。

分级冷凝是对生物油在线分离的手段之一,有研究人员通过研究水蒸气的冷凝特性来研究生物油的冷凝特性^[11-16],发现冷凝液膜热阻以及不可凝气体热阻影响着冷凝过程,KIRAN 等^[17-19]通过欧拉方法对生物质快速热解气中 11 种主要成分的水冷间接接触式冷凝传质过程进行了数值模拟,建立了气液两相的多组分传质模型,结果表明,不同组分在不同冷凝时间的冷凝效率不同。MOHAN 等^[20-23]研究表明:分级冷凝技术可以有效收集生物油,提高生物油的品质,因此研究生物油在不同冷凝温度区间的冷凝特性,对于有针对性地在在线收集生物油有理论和应用价值。

目前,针对生物质热解挥发物冷凝过程机理的研究较少,缺少生物油冷凝基础参数研究,对冷凝过程中不凝气的影响、气液两相传热传质特性问题研究不足。本文针对木屑在不同热解温度下产生的挥发物冷凝特性进行测试,计算冷凝换热系数、冷凝液膜热阻和厚度,为热解挥发物冷凝工艺和装置的设计提供理论基础。

1 材料与方 法

1.1 实验原料

本文使用的生物质木屑原料采自广州市某木材厂,木屑原料进行干燥、粉碎和过 30 目筛处理后,经工业分析测得其含水率为 6.62%,灰分质量分数为 5.02%,挥发分质量分数为 75.06%,固定碳质量分数为 13.31%,量热仪测得其低位热值为 15.77 MJ/kg。

1.2 冷凝特性测试装置

热解挥发物冷凝特性测试系统如图 1 所示,该测试系统主要由连续热解部分、测试管及数据记录部分、冷却水部分和冷凝液处理及排气部分组成。其中,连续热解反应发生装置为华南农业大学生物

质能实验室自主研制的变螺距连续热解装置^[24]。

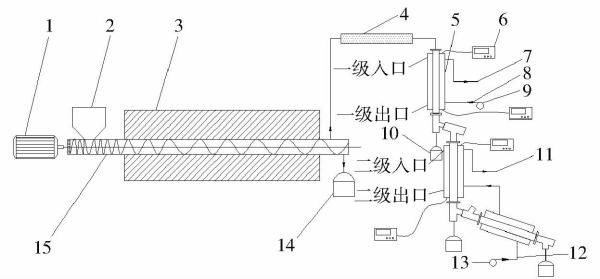


图 1 连续热解挥发物冷凝测试系统

Fig. 1 Condensation testing system for volatile matter of consecutive pyrolysis

1. 输送电动机 2. 入料料斗 3. 加热炉体 4. 粉尘过滤装置
5. 保温层 6. 温度传感器表头 7. 空气出口 8. 空气入口
9. 气泵 10. 取样瓶 11. 冷凝水出口 12. 冷凝水入口 13. 水泵
14. 炭箱 15. 变螺距螺旋输送机

冷凝测试系统由三级直型冷凝系统组成 ($\Phi 29$ mm/ $\Phi 24$ mm),前两级冷凝系统包括内管热解气测试部分、冷凝介质测试部分和温度传感器分布测试与数据采集部分,使用的传感器为 K 型热电偶,用于测定一、二级冷凝管进出口处(一级入口、一级出口、二级入口、二级出口,分别距离热解气入口 0.105、0.32、0.565、0.825 m)的热解气温度、冷凝管内壁温度、冷凝介质温度。

1.3 实验方法

在冷凝测试装置上对木屑进行热解温度为 450、550、650℃的冷凝测试实验,处理量为 1 kg/h。木屑原料通过连续热解装置热解后,产生的挥发分进入冷凝测试系统冷凝,不可凝气体由尾端排出。一级冷凝以空气作为冷凝介质,二级和三级冷凝则使用冷冻水,其中温度为 11℃的冷凝水质量流量为 1 200 kg/h,温度 25℃,空气质量流量为 4.257 kg/h。三级冷凝管的下端出口设置有生物油收集瓶,用以收集液态产物。

1.4 换热系数计算

冷凝系统局部表面换热系数由局部热流密度求出,局部热流密度通过冷却水侧的温度、流量和热流量求出,局部热流密度计算公式为^[25]

$$q(x) = \frac{mC}{\pi d_i} \frac{dT(x)}{dx} \quad (1)$$

式中 m ——冷凝介质质量流量

C ——冷凝介质的比定压热容, J/(kg·K)

T ——轴向位置 x 处测得的水温或气温,℃

d_i ——测试管内径, m

局部换热系数计算公式为^[26-27]

$$h(x) = \frac{q(x)}{T_b - T_{w,i}} \quad (2)$$

式中 T_b ——内管挥发物温度,℃

$T_{w,i}$ ——内管内壁温度,℃

1.5 液膜热阻及厚度计算

液膜热阻由热流量和液膜两侧温度差计算得到^[19],即

$$R = \frac{T_c - T_w}{q(x)} \quad (3)$$

式中 R ——冷凝液膜热阻, $m^2 \cdot K/W$

T_c ——冷凝管中热解气温度,℃

T_w ——冷凝管内壁温度,℃

液膜厚度通过生物油流体热导率和液膜热阻计算得到^[28-29],即

$$d = \lambda R \quad (4)$$

式中 d ——有效层流液膜厚度, m

λ ——流体热导率,取 $0.24 W/(m \cdot K)$

2 实验与结果分析

2.1 热解三态产率

热解三态产物产率如表1所示。随着热解温度的升高,炭产率减小;不凝气产率升高,在热解温度为 $650^\circ C$ 时达到最大值 60.02% ;生物油产率则随温度升高先升后降,在 $550^\circ C$ 时达到最大值为 42.82% ,挥发物含量随热解温度的升高而升高。

表1 不同热解温度时木屑的产物产率

Tab.1 Three states yield of sawdust pyrolysis %

温度/℃	炭	生物油	不凝气
450	37.51	33.05	29.44
550	23.96	42.82	33.22
650	18.83	21.15	60.02

前两级生物油产率如图2所示。随着热解温度升高,一级油产率逐渐减小,在热解温度为 $650^\circ C$ 时达到最小值 1.72% ;二级油产率则呈现先增后减的趋势,在热解温度为 $550^\circ C$ 时达到最大值 39.55% 。

2.2 换热系数计算结果

3个不同热解温度下的一、二级表面换热系数如图3所示。在 $450^\circ C$ 和 $550^\circ C$ 时,一级表面换热系数在实验前期波动较大,后期趋近于稳定, $650^\circ C$ 时

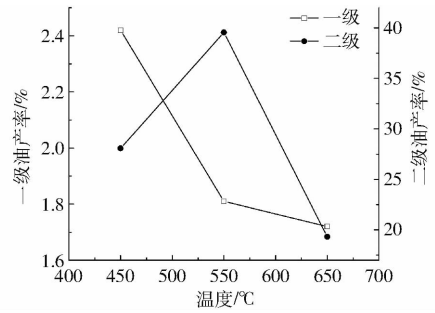


图2 各级油产率分析

Fig.2 Analysis of oil production at different levels

则全程呈现较大波动,这一现象也是木屑三态产物变化的直观表现, $650^\circ C$ 挥发物产率最大,且不可凝气体含量最大,产生这种情况可能是单独受到冷凝生物油或者不凝气的影响,也可能是二者的综合影响,同时, $450^\circ C$ 和 $550^\circ C$ 的一级油产率大于 $650^\circ C$,因此 $450^\circ C$ 和 $550^\circ C$ 时液膜更容易趋近稳定流动,维持稳定的局部换热系数;针对二级换热系数, $550^\circ C$ 时的二级油产率最大,因此更能形成稳定流动,其局部换热系数相比其他2个热解温度下的局部换热系数更趋于稳定, $650^\circ C$ 时热解挥发物中含有大量的不可凝气体成分,二级冷凝器中局部换热系数波动情况更严重。木屑热解挥发物冷凝平均局部表面换热系数如图4所示。随着热解温度升高,一级换热系数逐渐减小, $450^\circ C$ 时为 $671.02 W/(m^2 \cdot K)$,高于 $550^\circ C$ 时的 $402.89 W/(m^2 \cdot K)$ 和 $650^\circ C$ 时的 $380.20 W/(m^2 \cdot K)$;二级换热系数先增加后减小, $550^\circ C$ 时取得最大值 $1.484 \times 10^5 W/(m^2 \cdot K)$,高于 $450^\circ C$ 和 $650^\circ C$ 的相应值。由此可见,冷凝换热存在最大值,当超过冷凝换热最大值时,继续升温增加热解气的流量,不能对热解气中的可凝成分进行有效的冷凝。

3 液膜模型及分析

3.1 液膜模型

根据平壁一维稳态传热的结论^[19],忽略液膜可能存在的对流传热以及辐射传热,热解气在冷凝器中冷凝时,首先在壁面上形成液珠,当冷凝量较大

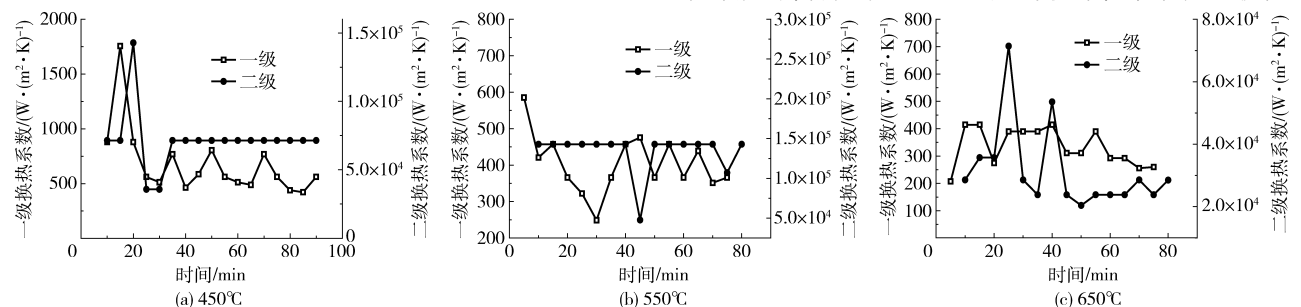


图3 冷凝器局部表面换热系数

Fig.3 Local surface heat transfer coefficient of condenser

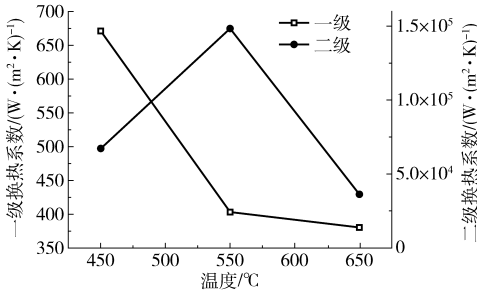


图4 木屑热解挥发物冷凝平均局部表面换热系数

Fig.4 Average local surface heat transfer coefficient of sawdust pyrolysis volatiles condensation

时,液珠向下流动积累,最终在壁面上积累形成一层液膜。液膜冷凝过程分为:液膜形成、液膜积累、液膜流动3个阶段,如图5所示。

3.2 液膜热阻及厚度计算结果

液膜热阻计算结果如图6所示。各个位置的冷凝液膜热阻随着实验的进行呈现波动状态,说明随着热解的进行,热解气中的可凝成分在不断变化,使得同一个位置上的液膜热阻不断变化,液膜厚度也相应不断变化。相同热解温度下,一级出口热阻大

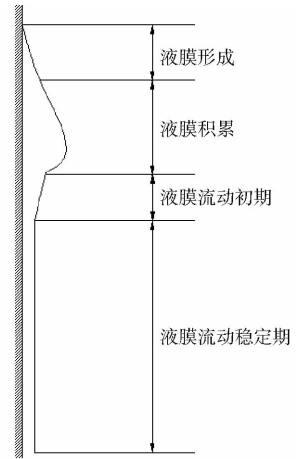


图5 热解气冷凝液膜形成过程示意图

Fig.5 Schematic of formation process of pyrolysis gas condensate film

出口的冷凝液流量比一级入口冷凝液流量大;二级出口热阻小于二级入口热阻,且更加稳定。二级使用水冷,冷凝效果好,在二级入口处已经有大量液珠的冷凝情况出现,在二级出口时,由于冷凝液流量大,因此流动状态更稳定,热阻也更为稳定。

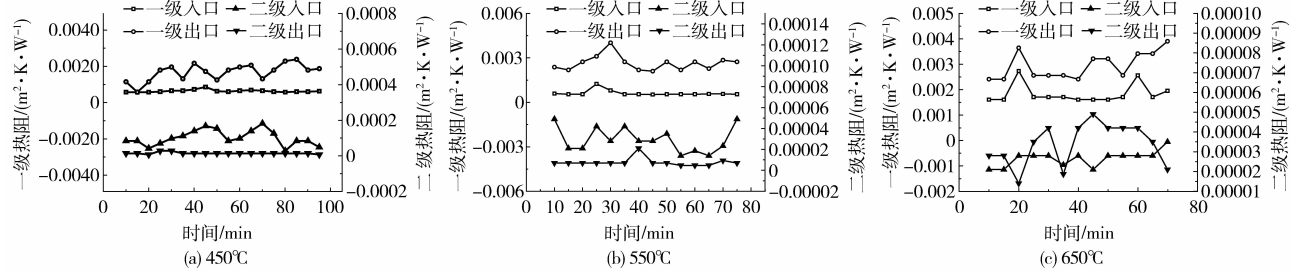


图6 不同热解温度下木屑热解挥发物的冷凝液膜热阻

Fig.6 Thermal resistance of condensation liquid film of sawdust pyrolysis volatiles at different pyrolysis temperatures

液膜热阻随着位置的变化如图7所示。木屑热解挥发物在不同热解温度下的冷凝热阻随位置的变化趋势一致,呈现先增加后减小趋势。由式(4)可知,液膜热阻和液膜厚度随位置的变化趋势相同,热阻和厚度增加段对应液膜形成阶段和液膜积累阶段,热阻和厚度减小段对应液膜流动初期。在650°C时,二级入口液膜热阻为 $2.68 \times 10^{-5} \text{ m}^2 \cdot \text{K}/\text{W}$,二级出口为 $3.30 \times 10^{-5} \text{ m}^2 \cdot \text{K}/\text{W}$,对应液膜厚度分别为 $6.69 \mu\text{m}$ 和 $8.25 \mu\text{m}$,热阻近似相等,说明在650°C时,二级入口和二级出口之间的流动接近液膜流动稳定期。

4 结论

(1)随着热解温度不断升高,冷凝器的一级换热系数减小,在热解温度为450°C时达到最大值 $671.02 \text{ W}/(\text{m}^2 \cdot \text{K})$,二级换热系数先增后减,550°C时达到最大值 $1.484 \times 10^5 \text{ W}/(\text{m}^2 \cdot \text{K})$ 。对比一级和二级油产率,与换热系数的变化趋势相同,说明在

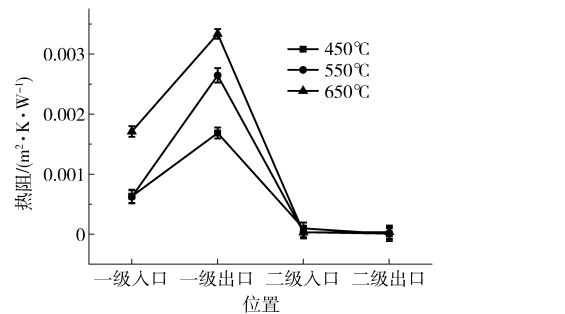


图7 不同热解温度下木屑热解挥发物的冷凝液膜平均热阻

Fig.7 Average thermal resistance of condensation liquid film of sawdust pyrolysis volatiles at different pyrolysis temperatures

一定的实验条件下,冷凝器的冷凝能力存在最大值,当热解挥发物流量超过冷凝能力最大值时便无法进行有效的冷凝。

(2)运用本文建立的冷凝液膜模型,对实验值进行计算的结果表明,生物油在冷凝管中的冷凝符合建立的液膜模型,存在液膜形成、液膜积累、液膜流动3个阶段。在液膜形成阶段,液膜厚度

开始增加,热阻逐渐变大;在液膜积累阶段,液膜厚度逐渐变薄,液膜热阻逐渐变小,距离足够时,流动持续变厚,热阻持续变大,直到积累到极限厚度,流动进入稳定期,液膜厚度基本不变,液膜热阻基本静止状态开始转为流动状态;在流动初期,液膜厚度不变。

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